CHLORO NITROSO TERPENES AND THE COTTON EFFECT

with an additional paper on

PHOTOCHEMICAL EXPERIMENTS WITH NITROSYL CHLORIDE.

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C O N T E N T S

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THE COTTON EFFECT AND ASYMMETRIC PHOTOLYSIS.

(A) The Cotton Effect.

Pasteur[1] has shown that a centre of dissymmetry (not necessarily an asymmetric atom) is required before a substance can exhibit optical activity, but he was unable to predict anything regarding the magnitude of the rotation. He pointed out, moreover, that an optically active substance had never been obtained, hitherto, without the intervention of life and asked some pertinent questions on the possibility of obtaining asymmetric syntheses by non-living asymmetric forces such as that of light.

Since the study of the Cotton Effect has provided the data for the modern insight to these questions, it is as well to consider it in some detail. The work of this thesis concerns the second problem, which, expressed in other words, is the production of optical activity in an inactive substance by a non-vital asymmetric force in this case circularly polarised light.

Optical Rotatory Power, or the rotation of plane polarised light on passing through an active medium was first fully investigated by Biot[2], whose classical experiments are described in five memoirs presented to the Academie des Sciences from 1812 until 1838.

That optical rotatory power is due to a small difference in circular double refraction was demonstrated by a contemporary of Biot's - Fresnel[3] - who considered that plane polarised light entering an optically active medium was split into two circularly polarised rays, one right-handed and the other left-handed. These two rays travelled at different speeds so that a phase difference (δ) arose between them. Recombination on leaving the medium again produced a plane polarised ray but the plane of polarisation had been rotated through an angle $\alpha = \frac{\delta}{2}$. Whether the light was rotated to the left or to the right depended on the relative speeds of the two circularly polarised rays. One enantiomorph, the laevo say, would rotate the plane of polarisation to the left and the dextro to the right. It can be easily shown that the difference in refractive indices of the two types of circularly polarised light need only be very small (1 part in a million) to produce a large rotation[4]. The relevant equation connecting refractive indices with rotation is:-

$$\alpha = \frac{\pi}{\lambda}\left(n_\ell - n_r\right) \qquad \text{-------} \quad (1)$$

is in degrees, n_l and n_r are the refractive indices of right handed and left handed circularly polarised light.

It will be seen that (λ), the wavelength of light, enters the equation so that it is of interest to see how α varies with λ.

As early as 1817 Biot[5] had recognised that rotatory power is roughly inversely proportional to the square of the wavelength, i.e., $\alpha = \frac{k}{\lambda^2}$ ------- (2) He was able thus to construct diagrams of Rotatory Dispersion showing the change of rotation with wavelength. It was soon, however, discovered that the Law of Inverse Squares was only approximately correct and that anomalous rotatory dispersion was more often the rule than the exception. This was especially the case with tartaric acid[6]. Biot's equation was accordingly modified by several workers, but the first satisfactory equation which was also based on theoretical considerations was given by Drude[7].

Drude based his equation on the hypothesis that absorbent media contain charged particles which possess natural periods of vibration. These are set into more or less violent oscillation when the frequency of the light impinging on the medium coincides with the natural frequency of the particles. Also, in a dissymmetrically isotropic medium the paths of these particles are helices and not straight lines so that optical activity will arise. These ideas are based on the Electromagnetic theory of Maxwell.

Drude's Equation is $\alpha = \sum \frac{k}{\lambda^2 - \lambda_o^2}$ ------- (3), where α is the rotation produced, and λ_o is the wavelength of maximum absorption.

Although this equation shows immediately that there must be a close connection between optical rotatory power and absorption, it failed to account for rotatory dispersion within an absorption band. It has, however, been effectively applied to optical activity in the region of transparency for many compounds.

Rotatory Dispersion in the Region of Absorption. What happens to optical activity in the region of absorption had already been observed experimentally by Cotton[8]. As rotatory power is really circular double refraction, is it not very similar to crystalline double refraction? Biot[9] had already observed that in tourmaline the extraordinary ray and the ordinary ray are absorbed to different extents, so Cotton deemed it not unjustifiable to assume that a medium might exist in which right- and left-handed circularly polarised light would also be absorbed to different extents.

He was able to demonstrate this effect with a 10 per cent solution of potassium chromium tartrate where he showed that in a 1 cm. length of solution the amplitude of a left-handed circularly polarised ray at the wavelength of maximum absorption was reduced to the extent of 91.2 per cent, while a right-handed ray of the same wavelength was reduced

by 92.3 per cent. This phenomenon he called CIRCULAR DICHROISM and it is now represented as $(\varepsilon_l \sim \varepsilon_r)$, where ε_l and ε_r are the Molecular Extinction Coefficients for right- and left-handed light. Proceeding from the position of maximum absorption the difference between ε_l and ε_r fell off rapidly, becoming zero in the region of transparency. Thus in the region of an optically active absorption band the two circularly polarised rays as well as travelling at different speeds are also unequally absorbed.

Ellipticity. Arising from this unequal absorption it follows that not only is the emergent ray rotated but it is also elliptically polarised and like circular dichroism the ellipticity rises to a maximum in the middle of the absorption band. It is usually expressed as

$$\tan \phi = \frac{a_r - a_l}{a_r + a_l} \qquad \text{---------- (4)}$$

where a_r and a_l are the amplitudes of the right- and left-handed rays respectively. Provided ϕ is small and substituting extinction coefficients for amplitudes this equation can finally be shown to become

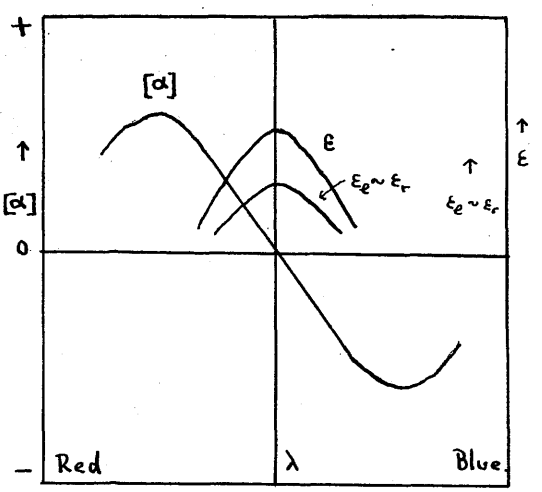
$$\phi = \frac{cl\,(\varepsilon_l \sim \varepsilon_r)}{4 \log 10} \quad \text{(in radians) ------ (5)}$$

Thus if ϕ is measured $(\varepsilon_l \sim \varepsilon_r)$ can be calculated.

Later on in this thesis (page 78) a direct method for detecting $(\varepsilon_l \sim \varepsilon_r)$ is described. The Ellipticity method has been developed by Bruhat[10].

Rotatory Dispersion. Cotton naturally investigated the rotatory dispersion in the region of absorption and was the first to show the peculiar anomalous behaviour of the rotation here. In the case of potassium chromium tartrate the rotation rose to a maximum on the long wave side of the absorption band, fell to zero in the centre and reached a minimum on the short wave side, thereafter the rotation decreased rapidly towards the violet end of the spectrum. The three effects, circular dichroism, absorption and rotatory dispersion, are shown in the diagram. These phenomena, taken together, are now known as the Cotton Effect.

Anisotropy Factor. Cotton also showed by his results on a solution of sugar coloured with magenta that an absorption band need not necessarily be active so that although circular dichroism cannot occur except in a region of absorption there is no quantitative relationship between them. The activity of an absorption band can be conveniently represented by the Anisotropy Factor



$$'g' = \frac{\varepsilon_e \sim \varepsilon_r}{\varepsilon} \qquad \text{----------} \quad (6)$$

i.e., circular dichroism divided by absorption; the greater

the circular dichroism and the smaller the absorption then the greater will be the rotation in the region of absorption.

It will be seen later that the factor 'g' is of the highest importance in asymmetric photolysis, the greater 'g' is the greater will be the optical activity induced in the racemic mixture.

Mathematical Relation Between Circular Dichroism and Rotatory Dispersion. Following from Cotton's results Drude [11] in 1906 modified his equation to account for the effect in the region of absorption. He introduced a Friction coefficient into the equation similar to the Damping Factor produced by Helmholtz[12] and Ketteler[19] in their equations connecting absorption with refractive index. Drude's expression was not, however, in convenient form and it was Natanson who in 1909[13] produced equations for both Circular Dichroism and Rotatory Dispersion. These are:-

$$n_\ell \sim n_r = \frac{D\lambda\left(\lambda^2-\lambda_o^2\right)}{\left(\lambda^2-\lambda_o^2\right)^2+\Gamma^2\lambda^2} \quad (7a) \text{ or} \qquad \alpha = \frac{D'\left(\lambda^2-\lambda_o^2\right)}{\left(\lambda^2-\lambda_o^2\right)^2+\Gamma^2\lambda^2} \quad (7b)$$

$$K_\ell \sim K_r = \frac{D\Gamma\lambda^2}{\left(\lambda^2-\lambda_o^2\right)^2+\Gamma^2\lambda^2} \quad (8a) \text{ or} \qquad \varphi = \frac{D'\lambda}{\left(\lambda^2-\lambda_o^2\right)^2+\Gamma^2\lambda^2}$$

n is the refractive index and k is the absorption index defined as $\frac{I}{I_o} = e^{\frac{-4\pi\kappa d}{\lambda}}$ D is a constant, Γ is a damping factor having the dimensions of a wavelength, embodying the half width of the absorption band.

These relations show remarkable similarity to those deduced earlier by Helmholtz and Ketteler to account for refractive dispersion in the region of absorption and the analogy between these two sets of phenomena is easily seen. For comparison these formulae are given below.

$$n^2 - 1 = \frac{D\lambda^2(\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2 + \Gamma^2\lambda^2} \qquad \text{-------- (9)}$$

$$2\pi k = \frac{\delta\Gamma\lambda^3}{(\lambda^2 - \lambda_0^2) + \Gamma^2\lambda^2} \qquad \text{-------- (10)}$$

Anisotropy Factor and Wavelength.

From the equations of Natanson and Helmholtz two points of interest arise:- First, that Anisotropy factor within an absorption band depends on wavelength.

From equations (8a) and (10)

$$g = \frac{K_\ell \sim K_r}{K} \propto \frac{1}{\lambda} \qquad \text{-------- (11)}$$

(substituting $\frac{K_\ell \sim K_r}{K}$ for $\frac{\epsilon_\ell \sim \epsilon_r}{\epsilon}$) provided that λ_0 and Γ have the same values, i.e., that the maxima of circular dichroism and absorption agree and that also the half widths of the bands are the same.

Natanson's and Bruhat's Rules connecting Rotation and Circular Dichroism.

The second point arises from equations (7b) and (8b). By dividing these Natanson evolved a rule connecting the sign of ellipticity with rotation

$$\frac{\alpha}{\varphi} = \frac{\lambda^2 - \lambda_0^2}{\Gamma\lambda} \qquad \text{---------- (12)}$$

when $\lambda > \lambda_0$ α and φ must always be positive and when $\lambda < \lambda_0$ α and φ must be of opposite signs.

"Thus on the long wave side of an optically active absorption band the sign of the elliptical vibration must be the same as the rotation, while on the short wave side the sign of the ellipse is of opposite sign to the rotation". (Lowry, "Optical Rotatory Power", p.427).

This rule is very useful in practice and in the present work has been applied to (-)-2-chloro-2-nitroso camphane where φ is negative, thus ε_r is greater than ε_ℓ and also to the pyridine salt of (+)-2-chloro-2-nitroso camphane-10-sulphonic acid, where φ is positive and hence ε_ℓ is greater than ε_r here.

From these equations Bruhat[14] also evolved a rule which stated "that for a narrow absorption band, the difference between the rotation maxima and minima is approximately equal to the maximum ellipticity φ ."

Calculation of Rotatory Dispersion from Circular Dichroism.

From Natanson's equations it will be seen that it should be possible to calculate the partial rotatory power due to an optically active absorption band since Γ is numerically equal to the half width of the curve of circular dichroism ($\kappa_\ell \sim \kappa_r$) and $D = \Gamma (\kappa_\ell \sim \kappa_r)$. Natanson[13]

himself obtained fair agreement when calculating the rotatory dispersion of Cotton's potassium chromium tartrate from circular dichroism figures.

Natanson's Equations can be applied only when the absorption band is very narrow. By using eight components Wedeneewa[15] was able to produce a theoretical curve approximating closely to the experimental details for camphorquinone.

The assumptions made by Drude for the original equations of Rotatory dispersion have been criticised by Born[16] and later by Kuhn[17], who based his ideas on a special case of Born's coupled resonators. Kuhn deduced an equation which although based on different assumptions is identical in form for a single characteristic wavelength with that of Natanson (equation 7b). In this equation D contains factors dependent on the amount of absorption and on the anisotropy factor 'g'.

In order to apply this to broad absorption bands it is necessary to consider some of the equations evolved for absorption.

Application to Broad Absorption Bands.

Bielecki and Henri[18] applied Ketteler's[19] modification of the Helmholtz equation (12) to experimental absorption curves and found that there was agreement only at certain

wavelengths near the maximum absorption. Much better agreement was obtained when they used an empirical equation of the form:

$$\varepsilon = \alpha\upsilon e^{-\beta(\upsilon_0 - \upsilon)^2} \qquad \text{---------- (13)}$$

where $\alpha = \varepsilon_{max}/V_0$. β is a constant embodying the half width of the band.

This equation has been modified by Kuhn and Braun[20] to

$$\varepsilon = \varepsilon_0 e^{-\left(\frac{\upsilon_0 - \upsilon}{\theta}\right)^2} \qquad \text{---------- (14)}$$

where θ is a parameter obtained from the frequency interval (v') between the points where ε is half ε_0. θ can be found from $v' = 1.6651\theta$.

Lowry and Hudson[21] have shown that absorption curves are usually more symmetrical on a wavelength rather than on a frequency scale, so that they employed this equation as

$$\varepsilon = \varepsilon_0 e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \qquad \text{---------- (15)}$$

From the similarity between absorption curves and dichroism curves (Equations (7), (8) and (11)), similar equations for dichroism were evolved,

Kuhn and Braun's being

$$(\varepsilon_\ell - \varepsilon_r) = (\varepsilon_\ell - \varepsilon_r)_0 \frac{\upsilon}{\upsilon_0} e^{-\left(\frac{\upsilon_0 - \upsilon}{\theta}\right)^2} \qquad \text{---------- (16).}$$

and Lowry and Hudson's being

$$(\varepsilon_\ell - \varepsilon_r) = (\varepsilon_\ell - \varepsilon_r)_0 \frac{\lambda_0}{\lambda} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \qquad \text{---------- (17).}$$

Kuhn and Szabo[22] in the case of potassium chromium

tartrate omitted the factor $\frac{v}{v_o}$ and obtained better results. This idea similarly applied to the equation of Lowry and Hudson gave

$$(\varepsilon_e - \varepsilon_r) = (\varepsilon_e - \varepsilon_r)_o e^{-\left(\frac{\lambda - \lambda_o}{\theta}\right)^2} \qquad \text{------- (18).}$$

Equations (15) and (18) have been applied with fair success to two compounds described in this thesis, namely, (-)-2-chloro-2-nitroso camphane and (+)-2-chloro-2-nitroso camphane-10-sulphonic acid.

Application to Rotatory Dispersion.

Since Natanson's equations apply only to narrow absorption bands, it was thus necessary to modify his equations in a similar manner to the equations of circular dichroism and absorption. Kuhn and Braun therefore modified their equation and arrived at an expression which, when integrated over the absorption band, gave the result:

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{(\varepsilon_e - \varepsilon_r)_o}{\log_{10} e} \cdot \frac{v}{v_o} \cdot \left[e^{-\left(\frac{v_o - v}{\theta}\right)^2} \int_0^{\left(\frac{v_o - v}{\theta}\right)^2} e^{x^2} dx + \frac{\theta}{2(v_o + v)} \right] \qquad \text{--- (19)}$$

$[M]$ being the partial Molecular Rotation associated with the band and θ a parameter embodying the half width of the band. When dichroism data are not available the equation may be applied by giving an arbitrary value to $(\varepsilon_e - \varepsilon_r)$ and employing values for v_o and θ from the absorption curves. Kuhn did this when applying this equation to the dimethyl amide of α-azidopropionic acid.

In the cases where this equation has been used, fairly good agreement between experimental and theoretical results have been obtained.

As before, Lowry and Hudson[21] used wavelengths instead of frequencies giving the equation as

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{(\varepsilon_e - \varepsilon_r)}{\log_{10} e} \cdot \frac{\lambda_0}{\lambda} \left[e^{-\left(\frac{\lambda-\lambda_0}{\theta}\right)^2} \int_0^{\left(\frac{\lambda-\lambda_0}{\theta}\right)^2} e^{x^2} dx + \frac{\theta}{2(\lambda_0+\lambda)} \right] \text{---- (20)}$$

Lowry and Hudson have used this equation to calculate partial rotations of a number of compounds.

Although good results have been obtained, particularly with xanthates, residual rotations were not quite free from anomalies. It is interesting to compare the results of Kuhn and Braun's equation and that of Lowry and Hudson for diphenyl l-menthyl dithiourethane (Lowry, p.446)* and for tetra-acetyl-μ-arabinose (Lowry, p.448)*.

Mathieu and Rayanette[23] found fairly good agreement for the rotatory dispersion curves of cyanocamphor using this equation.

In the case of chloronitroso compounds, Mitchell and Simpson[24] found very good agreement in calculating the partial rotations due to the -NO group for l-menthyl α-β-chloro-β-nitrosobutyrate and recently Mitchell and Naismith[25] have also been successful with (-)-γ-chloro-γ-nitroso-δ-phenylvaleric acid.

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*Lowry, "Optical Rotatory Power", Cambridge, 1935.

In the present work the equation has been applied with a fair degree of success to (-)-2-chloro-2-nitroso camphane and to (+)-2-chloro-2-nitroso camphane -10-sulphonic acid. In both cases practically the whole of the rotation in the visible region is due to the NO group.

Since the advent of Kuhn's Equation in 1930 some other equations have been advocated based on later theories of optical activity. Although quantum mechanical treatment has to some extent replaced the classical interpretation of optical activity, it has not given results suitable for practical application. It may be mentioned that Condon, Altar and Eyring[26] have shown on the basis of quantum mechanics that the motion of a single electron can give rise to optical activity in contrast with Kuhn's theory of coupled resonators. They applied this theory with some success to the case of methyl phenyl carbinol nitrite.

However, none of the later theories give a complete explanation of the theory of optical activity and although the process of approximation to the ideal equation is not yet complete, the equation of Kuhn and Braun seems to give the most satisfactory results.

(B) Asymmetric Photolysis.

Asymmetric Decomposition. From the foregoing discussion it has been shown that circular dichroism implies the unequal absorption of the two forms of circularly polarised light by an optically active medium. It thus follows that in a racemic mixture containing both enantiomorphs, one isomer will absorb one type of circularly polarised light more than the other isomer. No separation will occur by this difference alone but if in addition the light decomposes the substance, then one isomer will decompose at a different rate from the other, and the result will be the production of a certain amount of optical activity.

Although this idea was postulated by van 't Hoff in 1894[27], it was only successfully realised in 1930 by Kuhn[28] and Mitchell[29].

The photochemical decomposition of a substance will occur only if the light is absorbed. This is perhaps the first law of photochemistry and is due to Grotthus and Draper[30]. It would therefore appear that the greatest effect would occur in the region of an absorption band and as this should also be the region of circular dichroism, we should expect the maximum amount of selective decomposition occurring here.

Cotton[31] in his attempt to induce activity in copper

racemate by exposing it to circularly polarised light at the red end of the spectrum was unable to obtain any rotation after decomposition. This was due to the fact, as Byk[32] showed later, that the substance is not decomposed by red light, but by ultra violet light. Mitchell[33] also later demonstrated that in this region there is no circular dichroism for copper d-tartrate. An asymmetric decomposition of the tartrate could therefore not be expected.

Many other attempts were made during the period 1896 to 1930 to produce optical activity from racemic compounds by means of circularly polarised light, but there were all fruitless, mainly because some of the factors which add to give the conditions necessary for a successful photolysis were overlooked. These factors are now enumerated below.

Conditions necessary for Asymmetric Photolysis.

Before optical activity can be induced by means of circularly polarised light in any inactive substance, it must have the following characteristics:-

(1). No activity can be expected from an inactive substance unless the molecule is asymmetric although it need not contain an asymmetric atom. It is necessary therefore to start with a racemic mixture and if possible data on its active isomers should be known.

(2). The active form must exhibit a region of Circular Dichroism.

(3). The compound must be photo sensitive within the region of circular dichroism. Cotton's attempted resolution of copper racemate failed because the optically active band was not photo sensitive.

(4). A fourth necessary condition is that the Quantum Efficiency of the photochemical reaction should be in the region of 1.

This last condition means that there should be no subsidiary reactions occurring along with the absorption of radiation. Thus decomposition, without light (so-called dark reaction) would nullify the effect. A chain reaction, i.e., that initiated by light setting off other reactions, would also be most effective in destroying any asymmetry developed.

Quantum Efficiency (γ) is based on the Law of Photochemical Equivalence of Einstein[34] which states that a photochemical reaction takes place when a molecule exactly absorbs a quantum of energy. The quantum efficiency of a reaction would thus be unity. Thus the measure of a Quantum Efficiency would give a clue as to the suitability of a substance for asymmetric photolysis. If a chain or dark reaction occurred, then γ would be much greater than 1. If, on the other hand, the quantum efficiency is very much less than 1, then an asymmetric photolysis, though possible,

would be very tedious indeed.

If these conditions are satisfied, then an asymmetric photolysis should be possible, but the amount of rotation produced might be so small that it could not be detected. Thus other conditions are required in order that the rotation should be large enough, namely:-

(1). High Specific Rotation,

(2). High Anisotropy Factor 'g'.

(3). Destruction of asymmetric centre in the compound undergoing photolysis.

In order to calculate the amount of rotation produced Kuhn[35] has evolved an equation which depends among other things on $\gamma = 1$.

$$\alpha' = \frac{\alpha g}{2}\left(1 - \beta\right) \log \frac{1}{1-\beta} \qquad \text{-------- (21)}$$

where α' = rotation developed from a solution of the d:l-mixture,

α = rotation for a solution of pure d- or l-compound (conc. equal to the d.l. mixture at start).

g = anisotropy factor

β = degree of decomposition.

According to this equation Kuhn calculated that maximum rotation will be obtained at about 60% decomposition.

Even when all these requirements have been satisfied there are several other characteristics which it is desirable that the compound should have.

For ease in investigation of a Cotton Effect it should be situated in the visible region of the spectrum. From the point of view of taking readings of rotation of the photolysed compound this is a disadvantage but will be reduced if the extinction coefficient of the absorption is as low as possible. It is of interest to know also that the smaller the absorption is, the more likely is 'g' to be large[36].

Finally, for ease in extraction of the unchanged substance from its decomposition products it is an advantage if it is a solid.

Considering all these points it is quite understandable that there were so many fruitless attempts (see Mitchell's "Cotton Effect and Related Phenomena", London, 1933, p.60) before the final successful results of Kuhn and Mitchell.

The first successful attempt recorded was by Kuhn and Braun[37], who carried out an asymmetric photolysis of ethyl α-bromopropionate with circularly polarised ultraviolet light. A rotation of the order of 0.05° was obtained. Much better results were obtained by Kuhn and Knopf[28] who decomposed the dimethyl amide of α-azido propionic acid again using ultraviolet light. 37% decomposition with left-handed light gave a rotation of -1.04°, while a 35% decomposition gave a reading of $+0.78^{\circ}$ in 1 dm.

tubes. From the active dimethyl amide of α-azidopropionic acid, which had g = 0.024, Kuhn calculated from his equation that the induced activity at 40% decomposition should be $\alpha = 1.25^{\circ}$, in fair agreement with the practical results.

About the same time (1930) Mitchell[38], studying the Cotton Effect of caryophyllene nitrosite, observed that it had the very high anisotropy factor of 0.12, coupled with high specific rotations $[\alpha]_{6234} = +2207^{\circ}$, so that it was deemed very suitable for asymmetric work. Unfortunately the racemic form of caryophyllene is unknown, but the very similar sesquiterpene humulene is inactive. An asymmetric photolysis[29] on a 7% solution of this compound gave after 36 hours' irradiation with circularly polarised light in the region 6000 - 7000 Å $\pm 0.21^{\circ}$ at $\lambda = 5461$ Å. Additional readings at $\lambda = 5770$ gave rotations of $\pm 0.30^{\circ}$.

Similar results were obtained by Mitchell and Dawson[39], who photolysed a 4% solution of β-chloro-β-nitroso-α-δ-diphenyl butane, obtaining rotations of -0.10° and $+0.11^{\circ}$, and by Naismith[40], who obtained rotations of -0.07° for a 2% solution of β-chloro-β-nitroso-$\gamma\gamma$-dimethyl butane after 94% decomposition with left-handed circularly polarised light and $+0.11^{\circ}$ for a 3% solution after 94% decomposition with right-handed light.

In all these cases, however, the active substance was

not available to give data on the amount of rotation expected.

(2). Asymmetric Syntheses.

Although the work of this thesis is mainly concerned with asymmetric decomposition, it is of interest to note that there are references to asymmetric syntheses in which an optically active molecule has been built up from an inactive one by means of circularly polarised light. Karagunis and Drikos[41] chlorinated triaryl methyl radicals under the influence of circularly polarised light and obtained maximum readings of $\pm 0.07^{\circ}$.

Davis and Ackermann[42] performed the synthesis of ethyl d-tartrate from ethyl fumarate and hydrogen peroxide, the rotation produced here being 0.073°. Other asymmetric syntheses are reported by Davis and Heggie[43], Betti and Lucchi[44] and by Ghosh[45], but the rotations produced were all very small.

Although the amount of rotation produced from inactive substances by means of circularly polarised light has been very small, there is plenty of proof that the vital force suggested by Japp[46] is not necessary for optical activity. Byk[32] has shown that at the surface of the earth one kind of circularly polarised light is produced in excess by the reflection of the plane polarised sky light

under the influence of the earth's magnetism. This, then, acting for untold ages, may quite well have been responsible for some at least of the optical activity of natural products.

(C). Chloro Nitroso Terpenes and Asymmetric Photolysis.

The work of Kuhn on the dimethyl amide of α -azido-propionic acid and that of Mitchell on Humulene nitrosite proved beyond doubt that it was possible to produce optical activity in a racemic mixture using only circularly polarised light.

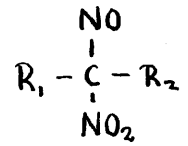
Both these compounds are, however, subject to certain limitations, so that it was thought desirable to prepare compounds whose properties more fully met the requirements.

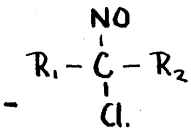
In order that calculation may be made as to the amount of optical activity induced by circularly polarised light in an inactive substance, it is necessary to prepare the compound in the active form. Although the dimethyl amide of α -azidopropionic acid is obtainable in both the active and inactive forms, this is not the case with humulene and as already stated, Mitchell used the data for the very similar terpene caryophyllene. A further point is that the structure of these two substances is still a matter of conjecture[47]. Nevertheless, caryophyllene nitrosite has very desirable features, the most noteworthy being that the Cotton Effect is conveniently situated in the visible part of the spectrum and this is a decided advantage over the dimethylamide of α -azidopropionic acid, where the active absorption band occurs about 2900 Å where rotatory dispersion measurements are decidedly difficult.

Another most important advantage is that the Anisotropy factor is very high, g = 0.12, in comparison with 0.024 for the dimethyl amide of α - azidopropionic acid. In many other ways caryophyllene nitrosite fulfils the requirements enumerated in the last part and its important properties are due mainly to the -NO group in the molecule. Considering these factors, Mitchell and his collaborators felt it expedient to investigate simpler compounds containing the nitroso group, but surprisingly enough, this proved to be a singularly difficult task.

The first of these studied was the simpler terpene, bornylene nitrosite[48]. The structure of this is known and it can be obtained both in the active and inactive forms. Mitchell and Cormack also investigated the nitrosites of phellandrene and zingiberine but these were unsuitable. These compounds have the disadvantage that they exist in the dimeric state at room temperature and are thus white compounds. They become blue only when heated. Bornylene nitrosite was the most suitable of the three, having g = 0.04, but even it was too unstable for asymmetric photolysis.

This work led to the preparation of pseudo-nitroles by Mitchell and Gordon[49]. In this case a nitro and a nitroso group are attached to the same carbon atom, e.g.,

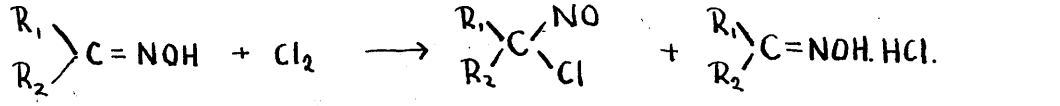
 so that photo-oxidation would destroy the asymmetric centre. It was soon found, however, that these compounds were subject to dark reactions which rendered asymmetric photolysis impracticable. These workers investigated camphor pseudo-nitrole with a view to asymmetric work, but found that it passed on oxidation without the influence of light to 2:2-dinitrocamphane[50].

It was an important step forward when attention was turned to chloro nitroso compounds of the type,  A number of these compounds had already been prepared, first by Piloty[51] and later by Rheinboldt and Dewald[52]. In almost every case they are blue and do not form dimers.

Lynn[53] found that nitrosyl chloride on n-heptane in presence of sunlight produced a transient blue colour which he thought was due to a secondary nitroso compound. He later showed[54] that oximes were produced in the reaction, but Mitchell and Carson[55], fully investigating the matter, showed that actually $\beta\beta$- and $\gamma\gamma$-chloronitroso hexanes were formed. Furthermore, red light in the absence of oxygen converted the chloronitroso compounds to oxime hydrochlorides, but that photo-oxidation occurred in the presence of oxygen.

Further work showed that the chloro nitroso group was

eminently suited for the work envisaged. The compounds can be easily made by the action of NOCl or chlorine on the ketoxime. The reaction may be shown as follows:-



the oxime hydrochloride, as a rule, redissolving to form more chloronitroso derivative.

Advantages of chloro nitroso compounds are many. They almost all exist in the monomeric form, i.e., they are blue. Their absorption bands (about 6500 Å) are conveniently situated in the visible region; their quantum yields are in the region of unity, and they normally decompose under the action of red light to give oximes when oxygen is absent. Mitchell and Cameron[56] have shown in their paper "The Photolysis of β chloro β nitroso butane" how suited these compounds are for asymmetric work.

In later trying asymmetric decompositions these contentions were proved and as already mentioned, positive results were obtained with β-chloro-β-nitroso- α-δ-diphenyl butane[39] and with β-chloro-β-nitroso- γγ-dimethyl butane[40].

However, this work gave only half the data required as no method of producing the pure optical isomers was known. It therefore became desirable to complete the investigation by producing the pure d or l isomer to obtain data for the furtherance of the subject. Thus it was

necessary (a) to resolve a racemic compound using the classical methods, or (b) to make an optically active chloro-nitroso compound from an optically active starting material. The second case would mean, of course, the introduction of a second asymmetric centre as the only known method (another possible method is given in the Additional Paper to this Thesis) is by acting upon the oxime with chlorine or nitrosyl chloride.

First attempts at case (a) were by Mitchell and Simpson[24], who made l-menthyl d- -chloro- -nitroso- butyrate. This, after about 6 crystallisations from ethanol, gave a good Cotton Effect, having the following characteristics:-

$[\alpha]_{5660}$ -415.4° $[\alpha]_{6600}$ +484.6° ε_{max} = 17.2

g = 0.038.

This compound did not completely satisfy requirements, however. It was impossible to remove the menthyl radical by hydrolysis leaving the simple compound, and furthermore it did not yield simple products when decomposed by red light. Nevertheless it paved the way for the final success which was the resolution by Mitchell and Naismith[25] of (-)- γ-chloro- γ- nitroso- δ-phenylvaleric acid, which was resolved by "(+)- β-naphthol-phenylaminomethane". [(+)- α-(2-hydroxyl-1-naphthyl)benzylamine.]

The only aspect now requiring investigation was the production of optical activity from the racemic mixture of a compound whose d or l isomer was of known rotatory dispersive power. This could have been attempted with (-)- γ-chloro- γ-nitroso- δ-phenylvaleric acid, but 'g' was only 0.023 and $[\alpha]_{6760}$ -400°; $[\alpha]_{5900}$ $+372^{\circ}$, so that the amount of induced rotation would have been rather small and difficult to detect.

In this thesis the object was to obtain a compound which had an Anisotropy Factor 'g' as high as possible and with as great rotation as possible. Such a substance must be easily obtainable in both the active and inactive forms - it should fulfil as many of the conditions for asymmetric photolysis as possible.

Two lines of approach were suggested:- (a) the production of an active blue compound from an active ketone. This, of course, would introduce at least another asymmetric centre, thus sacrificing simplicity. (b) The introduction of a nitroso group into an optically active secondary chloro compound.

Although it was found possible in case (b) to introduce the nitroso group in a manner similar to that of Mitchell and Carson[55] in a few compounds, it was impossible to produce an active chloronitroso compound in this manner. An

account of this work is given in the Additional Paper on "Photochemical Experiments with Nitrosyl Chloride" (page 84)

Method (a) has given very interesting results with terpenes of the camphor type.

Camphor itself was naturally the substance upon which investigations commenced. It is readily obtained both in the active and inactive forms, it is cheap, and readily forms an oxime. In the usual procedure this gave (-)-2-chloro-2-nitroso camphane which was found to have the remarkable anisotropy factor of g = 0.15, while $[\alpha]_{7000}$ was +946°; $[\alpha]_{6000}$ -964°. These high values were discovered only after some tedious work, but the results can now easily be duplicated. (-)-2-chloro-2-nitroso camphane has indeed been found to be an ideal substance to demonstrate the Cotton Effect in the visible region.

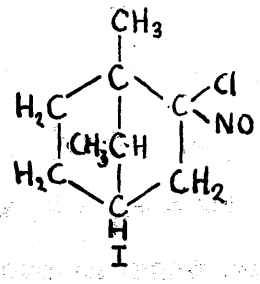
However, the decomposition of this compound by red light led to the curious result that a change of rotation was quickly produced. The substance thus seems to exist in two distereoisomers and the light initiated a change from one to the other. This made the compound unsuitable for asymmetric work, but the corresponding (+)-2-chloro-2-nitroso camphane-10-sulphonic acid was found free from this defect and a successful asymmetric decomposition was carried out on it.

After 60% decomposition of a 10% solution with circularly polarised red light from an arc lamp, rotations of +0.11 and-0.14° at λ_{5000} were obtained. These rotations are rather small, but they are sufficiently large to show that asymmetric photolysis had occurred to a certain extent.

Other chloro-nitroso terpenes exhibiting the Cotton Effect described in this thesis are 2-chloro-2-nitroso fenchane and 2-chloro-2-nitroso-isocyclene. The blue compounds corresponding to epicamphor and camphenilone were also made, but in too small quantities to warrant detailed investigation.

PHOTOCHEMISTRY OF 2-CHLORO-2-NITROSO CAMPHANE.

Although chloronitroso compounds of the type $R_1-\overset{Cl}{\underset{NO}{C}}-R_2$ are well known[52], it is curious that there is only one reference to a terpene derivative of this nature in the literature. Rimini[59], who was attempting to prepare pernitroso santenone (II) by the action of nitrous acid and hydrochloric acid on santenone oxime, obtained instead a blue oil (b.p. 113-116° at 9 m.m. pressure), whose formula has been represented as I



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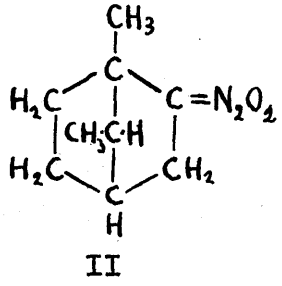


II

The action is unusual and no other chloronitroso compounds have been prepared in this manner: other oximes like that of camphor and fenchane give only the pernitroso compound, although all investigators[60] noticed the formation of a transient blue colour. This may be due to the momentary existence of a dinitroso isomer $=C\overset{NO}{\underset{NO}{\diagdown\diagup}}$ before rearrangement. There is still some doubt[61] as to the true configuration of these pernitroso compounds, but as the blue colour is transient, they are unsuitable for investigation in the present work.

On the other hand, the corresponding chloro-nitro and bromo nitro camphanes were prepared in 1899 by Forster[62], who considered at first that they must be nitroso derivatives because they gave Liebermann's Nitroso Reaction, but he was later forced to conclude that they were true nitro compounds. Forster made these substances by the action of sodium hypochlorite and hypobromite on camphor oxime. In the case of the nitro bromocamphane he noticed that a blue colour was produced but that this soon faded.

Preparation of 2-chloro-2-nitroso camphane.

This blue solid can be easily prepared from camphor-oxime by the general method evolved by Mitchell and Dawson[39] for chloro nitroso compounds.

When camphor oxime ($[\alpha]_D = -42^\circ$ in alcohol) is dissolved in sodium dried ether and chlorine gas is passed in, a yellow colour is produced. This turns green and after a time a deep blue-green. At the same time a white precipitate of oxime hydrochloride is formed, and this, unlike all other ketomime hydrochlorides treated in a like manner, does not redissolve with excess chlorine.

The reaction can be shown as follows:-

$$2\,C_{10}H_{16}{=}NOH + Cl_2 \longrightarrow C_9H_{16}{:}C\begin{matrix}NO\\Cl\end{matrix} + C_{10}H_{16}{=}NOH.HCl$$

Since the oxime hydrochloride is thus so much less soluble

than the blue compound, it will be seen that if a small amount of ether is used the hydrochloride will precipitate out and the blue compound can be easily isolated by evaporating off the ether.

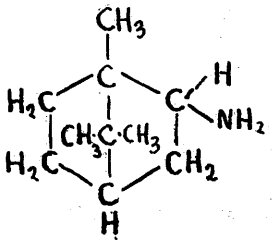
However, when made in this way (see Fig.I, Table I), although indeed a Cotton Effect was observed, it was disappointingly small, $[\alpha]_{6000}$ varying between $+100^{\circ}$ and $+200^{\circ}$ with correspondingly low rotation values for other wavelengths. Repeated recrystallisation of the blue solid from methanol failed to alter these results.

Di stereoisomers of 2-chloro-2-nitroso camphane.

Another asymmetric centre has been introduced into the molecule so that it was envisaged that two di stereoisomers might be present and furthermore these might have opposite rotations. This would explain the low rotation of the product.

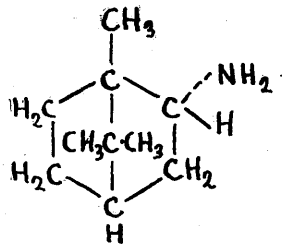
Examples of this as far as camphor is concerned are many. Suffice to say that bornylamine IV has $[\alpha]_{D} = +47.2^{\circ}$ in ethanol and neobornylamine III has $[\alpha]_{D} = -43.7^{\circ}$ in ethanol. Both are made from d-camphor. When d-camphor is converted by a Leuckart reduction[63] neobornylamine predominates in the mixture of the isomers, while the reduction by camphor oxime with sodium gives mainly the (+) isomer[64]. The two isomers can, however, be separated by means of their hydrochlorides which have very different

solubilities in alcohol.



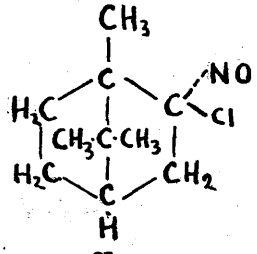
III

and

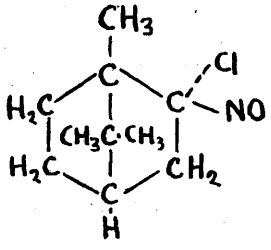


IV

It therefore seemed reasonable to assume that similarly two isomers of 2-chloro-2-nitroso camphane should also exist.



V



VI

The problem was now to separate these and produce one at least in a pure state. It has already been stated that fractional crystallisation had no effect.

However, a clue was given to a possible separation when it was discovered that using excess ether in the preparation just described gave a product with much larger rotation. This meant that some of the oxime hydrochloride was dissolving and taking part in the reaction. When finally the oxime hydrochloride was dissolved in ether a much more highly active compound was produced. This had $[\alpha]_{6000}$ +700° and the other rotations were correspondingly increased.

A final purification was achieved by chromatography.

The product described in the last paragraph was dissolved in a little 60-80° petroleum ether and passed through a column of alumina 1 cm. wide and 30 cm. long. This was eluted with more petroleum ether and the solid ultimately recovered crystallised from methanol. It will be shown later how sensitive the blue camphane is to red light so that all stages, particularly the last, have to be done in darkness as far as possible.

This final product has the following characteristics:-

Rotation:- $[\alpha]_{6000} = +964^{\circ}$; $[\alpha]_{7100} = -964^{\circ}$;
$[\alpha]_{6700} = 0.0$.

Absorption:- $\epsilon_{max} = 12.9$ at $\lambda = 6600$ Å.

Circular Dichroism:- $(\epsilon_l - \epsilon_r)_{max} = 1.14$ at $\lambda = 6700$ Å

Anisotropy Factor:- $g = 0.15$ at $\lambda = 7200^{\circ}$.

The melting point was fairly sharp at 127°C.

Analysis: Found, C = 59.61; H = 7.61; N = 6.85.

Calculated for $C_{10}H_{16}ONCl$, C = 59.55; H = 7.93; N = 6.93%.

It is very soluble in all the ordinary solvents but can be crystallised from methanol. The solid is insoluble in water and has a pungent odour reminiscent of other chloro nitroso compounds.

The evolution of the Rotatory Dispersion Curve is shown in figure (1) and Table I. Absorption and Circular Dichroism Curves are given in figures (5) and (6), Table II.

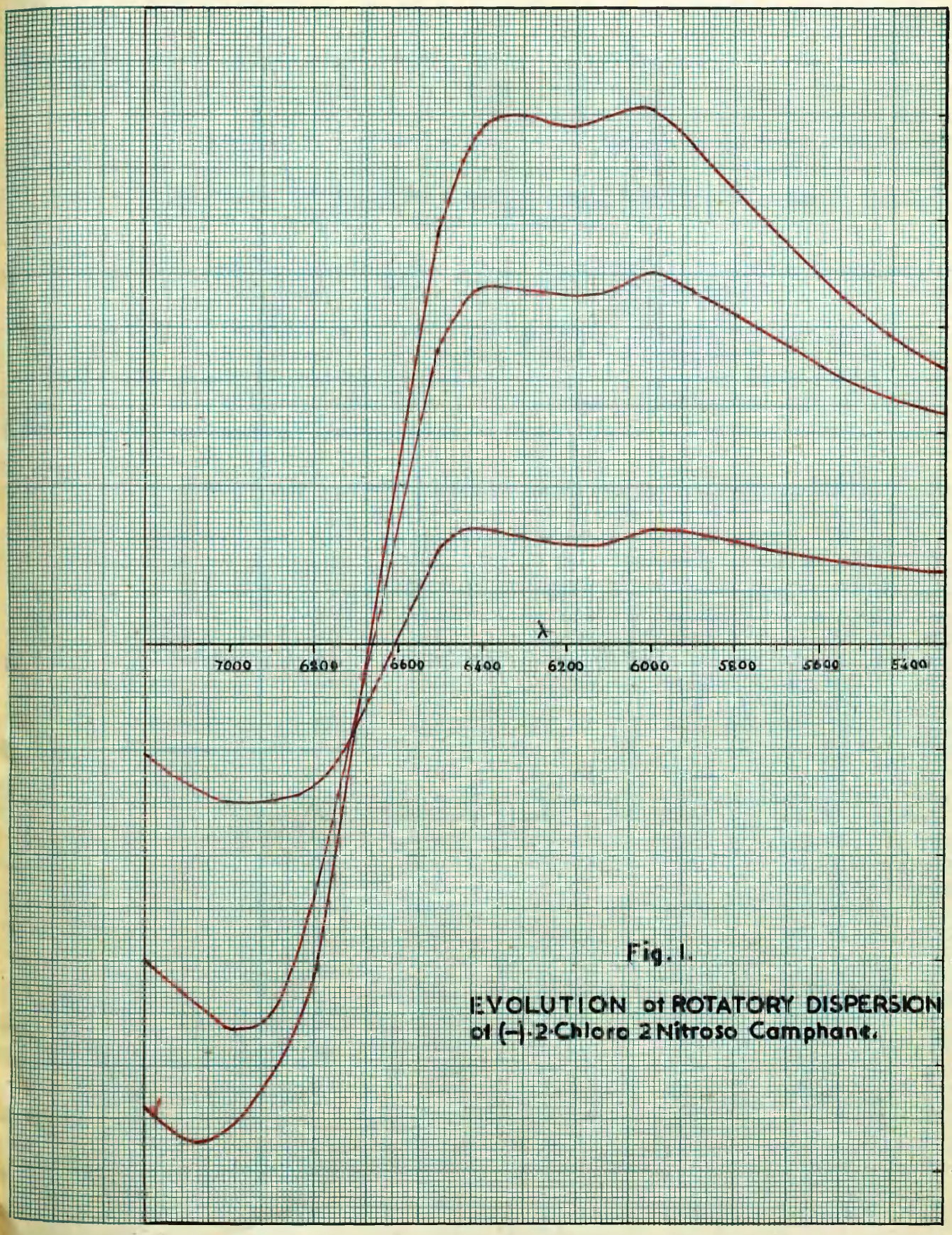


Fig. 1.

EVOLUTION of ROTATORY DISPERSION of (−)-2-Chloro 2 Nitroso Camphane.

Table I.

Rotatory Dispersion of (-)-2-chloro-2-nitroso camphane.

I. Made from camphor oxime using minimum amount of ether. c = 0.3333 g./100 ml. Ethanol.

II. Made from camphor oxime hydrochloride using large amount of ether. c = 0.302 g./100 ml. Ethanol.

III. Product from II after passing through chromatographic alumina. c = 0.280 g./100 ml. Ethanol.

All measurements taken in a 1 dm. polarimeter tube.

α and $[\alpha]$ in degrees.

	I		II		III	
λ	α	$[\alpha]$	α	$[\alpha]$	α	$[\alpha]$
4750	+0.28°	+84°	+0.89°	+296°	-	-
5000	+0.33	+99	+1.03	+343	+1.32°	+471°
5200	+0.37	+111	-	-	+1.44	+514
5400	+0.48	+144	+1.38	+460	+1.60	+571
5500	-	-	-	-	+1.90	+643
5600	+0.53	+159	+1.68	+526	+1.92	+686
5700	-	-	-	-	+2.16	+771
5800	+0.63	+189	+1.88	+626	+2.45	+875
5900	-	-	+2.01	+670	+2.65	+946
6000	+0.74	+222	+2.10	+700	+2.70	+964
6100	+0.62	+186	+1.98	+666	+2.65	+946
6200	+0.64	+192	+1.97	+660	+2.60	+924
6300	+0.69	+207	+1.97	+660	+2.65	+946
6400	+0.75	+225	+2.00	+670	+2.60	+929
6500	+0.60	+180	+1.68	+560	+2.15	+768
6600	0.0	0.0	+0.9	+300	+0.95	+339
6700	-0.62	-186	-0.51	-170	-0.05	-179
6800	-0.92	-276	-1.40	-460	-1.75	-625
6900	-0.95	-285	-2.10	-700	-2.25	-804
7000	-1.00	-300	-2.20	-730	-2.55	-911
7100	-	-	-	-	-2.65	-946
7200	-0.7	-210	-1.80	-600	-2.45	-875

Table II.

Circular Dichroism and Absorption of (-)-2-chloro-2-nitroso Camphane in Alcohol.

For ($\varepsilon_r - \varepsilon_e$) concn. = 0.0141 M ; l = 2.5 cm.

For ε concn. = 0.0680 M ; l = 1 cm.

λ	$\varepsilon_r - \varepsilon_e$	ε	g
5400	-	1.68	-
5600	-	2.65	-
5700	0.08	3.25	0.025
5800	0.10	4.15	0.024
5900	0.19	5.30	0.036
6000	0.30	6.45	0.047
6100	0.36	7.65	0.047
6200	0.47	8.70	0.054
6300	0.57	9.65	0.059
6400	0.64	11.50	0.056
6500	0.85	12.50	0.068
6550	0.94	12.90	0.073
6600	1.08	12.90	0.084
6650	1.14	12.50	0.091
6700	1.14	11.60	0.098
6800	1.06	8.90	0.119
6900	0.85	6.20	0.137
7000	0.55	4.10	0.134
7100	0.37	2.60	0.142
7200	0.27	1.80	0.150

The red line in each case shows the experimental results.

Evidence for Two Di stereoisomers of 2-chloro-2-nitroso camphane.

From the foregoing results it would appear that a separation of two distereoisomers is taking place and that camphor oxime hydrochloride gives a product in which there is a much greater preponderance of the (-) isomer. The chromatogram effects a further separation. The final product may of course still be slightly impure.

In order to substantiate this postulation of the two isomers, an attempt was made to find the second isomer and the following evidence is given in support of this contention.

(1). Action of chlorine on the oxime dissolved in pyridine.

Since bornylamine and neobornylamine can both be made from camphor by different reactions it was thought that by altering the experimental procedure evidence of a second isomer might be obtained.

When camphor oxime was dissolved in pyridine and cooled to $-10^{o}C$ addition of chlorine gave a green solution. This solution was extracted with ether, neutralised, and examined under the polarimeter. It showed anomalous rotatory dispersion: the curve was however in the opposite sense to that of (-)-2-chloro-2-nitroso camphane. The rotation however altered very quickly in the dark; in one

sample the rotation at λ = 6000 Å changed from -1.75° to -1.3° in one hour. (See Fig. 4. Table V).

As this mutarotation must have been occurring during the preparation it was impossible to find out the maximum activity of this species of blue compound. In about four hours an equilibrium position was reached (Fig. 4), after which the rotation did not change.

(2). A very interesting and curious phenomenon which is described in the next section is the effect on the rotatory dispersion when (-)-2-chloro-2-nitroso camphane is exposed to red light. Although this compound is free from dark reactions, red light very quickly alters the rotation which in the space of $2\frac{3}{4}$ hours changed from +2.30° to -0.88° at 6000 Å (for a particular specimen). A reverse Cotton Effect was produced. It would appear that both isomers tend to an equilibrium position, but owing to the inability in obtaining the (+) variety in a pure state, it has been impossible to verify this.

Photolysis of (-)-2-chloro-2-nitroso camphane.

Mitchell and Carson[55] have shown that in the presence of oxygen chloro-nitroso compounds oxidise to the corresponding nitro compound when irradiated with red light, although when oxygen is excluded the photolysis takes a different course. As a rule the oxime is formed and the asymmetric centre destroyed. This is of course an advantage for asymmetric photolysis.

In order to ascertain whether (-)-2-chloro-2-nitroso camphane would be suitable, it was decided first of all before embarking on a synthesis of the inactive form, to try a photo-chemical decomposition on the active material.

It would seem that the blue terpene would be very suited for this effect since g = 0.15 - a remarkably high anisotropy factor.

From Kuhn's equation

$$\alpha' = \frac{\alpha g}{2}(1-\beta)\log.\frac{1}{(1-\beta)}$$

α' = rotation developed from a solution of the dl mixture

α = rotation for solution of the pure compound

g = anisotropy factor

β = degree of decomposition.

Calculation has shown that 60% decomposition should give a maximum for α'

when $\beta = 0.6$ $\qquad \frac{\alpha'}{g\alpha} = 0.183$

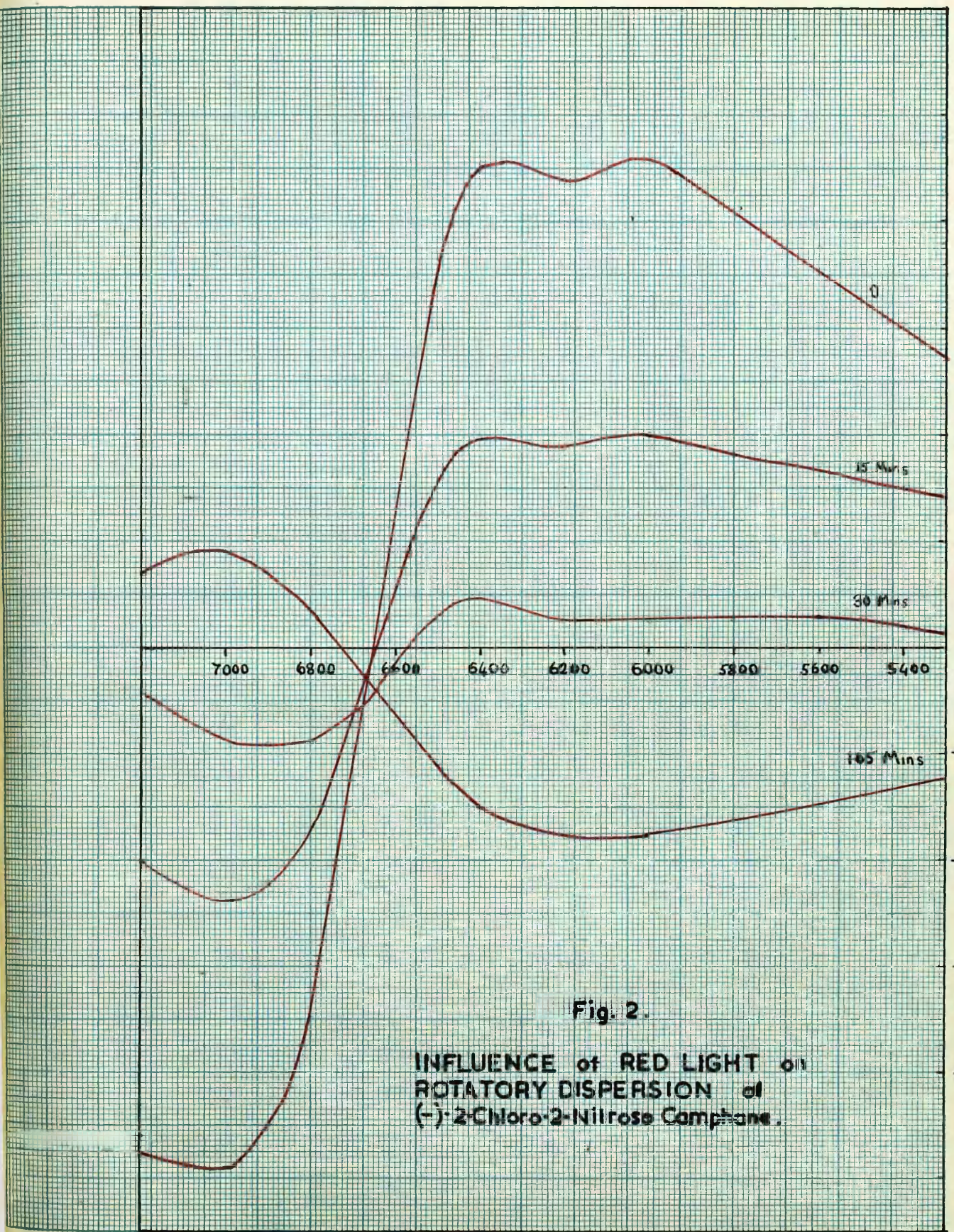


Fig. 2.

INFLUENCE of RED LIGHT on ROTATORY DISPERSION of (-)-2-Chloro-2-Nitroso Camphane.

Table III.

The Influence of Red Light on the Rotation of (-)-2-chloro-2-nitroso camphane.

Rotatory Dispersion at different time Intervals.

c = 0.024g. in 10 ml. Ethanol (oxygen free). A 1 cm. cell exposed to red light from 1000 c.p. Pointolite Lamp (250 v. D.C.).

Time in Minutes	Rotations in degrees			
λ	0	15	30	165
7400	-1.95	-0.65	-0.03	-
7200	-2.40	-1.03	-0.22	+0.35
7000	-2.45	-1.20	-0.45	+0.45
6900	-2.25	-1.10	-0.45	+0.35
6800	-1.75	-0.85	-0.43	+0.17
6700	-0.40	-0.35	-0.39	-0.05
6600	+0.70	+0.27	-0.04	-0.35
6500	+1.70	-	+0.13	-0.55
6400	+2.25	+0.97	+0.25	-0.75
6200	+2.20	+0.93	+0.13	-0.88
6000	+2.30	+0.98	+0.13	-0.88
5800	+2.03	+0.90	+0.13	-0.81
5600	+1.75	+0.85	+0.14	-0.75
5400	+1.53	+0.75	+0.10	-0.63
5200	+1.31	+0.58	+0.05	-0.55
5000	+1.15	+0.37	+0.0	-0.47

Fig. 3.

INFLUENCE of RED LIGHT on ROTATION of (-)2-Chloro-2-Nitroso Camphane.

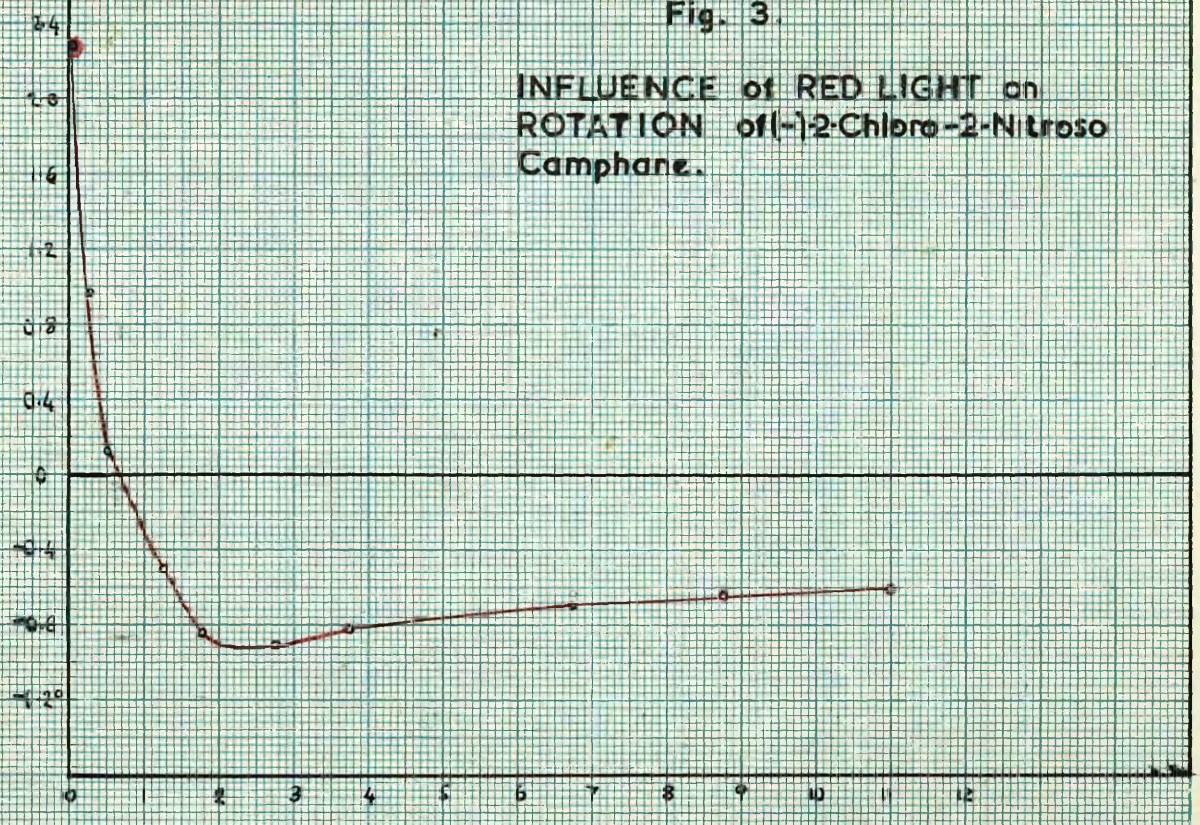
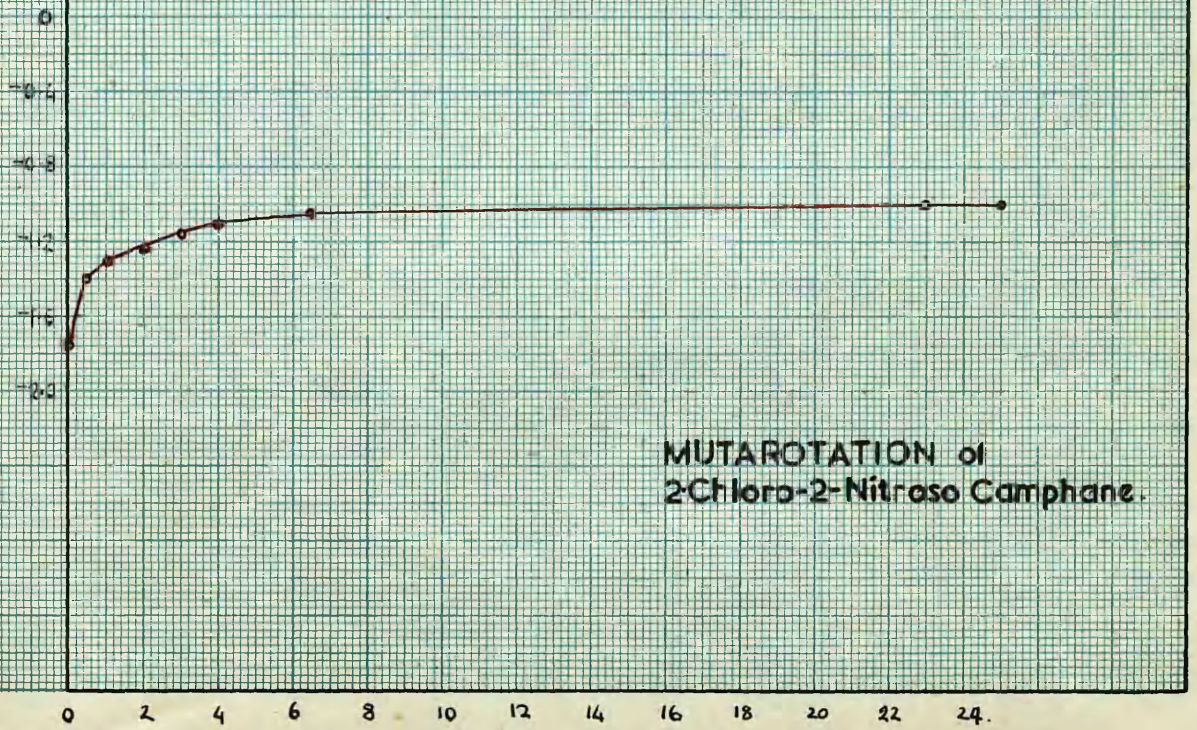


Fig. 4.



MUTAROTATION of 2-Chloro-2-Nitroso Camphane.

Table IV.

The Influence of red light on the Rotation of (-)-2-chloro-2-nitroso camphane.

Rotation at λ = 6000 Å at different time intervals. (1 cm. tube).

Time (hours)	Rotation
0	+2.30
0.25	+0.98
0.5	+0.13
1.25	-0.51
1.75	-0.84
2.75	-0.88
3.75	-0.81
6.75	-0.70
8.75	-0.65
11.0	-0.61.

Table V.

Mutarotation of Second Form of 2-chloro-2-nitroso camphane (dark reaction).

Rotations taken in 1 dm. tube at λ = 6000 Å.

Time (hours)	Rotation
0	-1.75
0.5	-1.4
1.0	-1.3
2.0	-1.24
3.0	-1.15
4.0	-1.10
6.25	-1.05
23	-1.00
25	-1.00

Thus for g = 0.15 and α = 20° (an easily read rotation at 6000 Å)

α' should be = 0.15 x 0.183 x 20

= <u>0.549°</u>.

Thus using both left- and right-handed circularly polarised light 60% decomposition of inactive 2-chloro-2-nitroso camphane should give rotations of ±0.5°. However, as already stated in the Introduction, many factors contribute to the success of an asymmetric photolysis and in this case one important factor, namely the Law of Photochemical Equivalence, was found to be invalid.

So that no oxidation would occur, a solution of (-)-2-chloro-2-nitroso camphane was dissolved in air free alcohol and exposed in a sealed cell 1 cm. long to red light from a 1000 candle power "Pointolite" Lamp. Between the lamp and the cell was interposed a red filter giving light from 6000 Å to 7000 Å and also a water-cooled filter to protect the blue solution from heat.

The results which were obtained are shown in Tables III and IV and graphed in Figs. (2) and (3).

In the course of half an hour the rotation (for one particular sample) had become zero and after $2\frac{3}{4}$ hours a Cotton Effect had been produced opposite in sign from the original one. During this period the absorption had not altered.

The following points are worthy of note:-

(1). When a solution of (-)-2-chloro-2-nitroso camphane was left in the dark there was no change in rotation even after several days.

(2). Exposure to blue light from a Mercury Arc Lamp had no effect on the rotation although 10 minutes' exposure to red light from the Pointolite lamp halved the rotation at 6000 Å. It was thought that once initiated by red light, blue light might cause the reaction to continue, but this also led to negative results.

(3). When carbon tetrachloride was used as solvent instead of ethanol no difference was noted in the rate of reaction.

(4). As will be seen from the figures in the table, the rotation changes very quickly from a positive value at 6000 Å to a negative minimum. Absorption measurements up to this point showed no change either in intensity or in the position of maximum absorption, i.e., at 6600 Å. There was then a fairly static position in which both rotation and absorption remained steady, but after this the absorption decreased in intensity and the rotation became less negative. Ordinary photolysis thus set in but the rate was extremely slow in comparison with the "photo mutarotation". Several days' irradiation were required before the solution became colourless.

No satisfactory explanation of these results has been deduced, but there seems to be little doubt that this is a case where one distereoisomer is being converted partially into the other by the effect of red light. It is the first case of "mutarotation" observed in the region of absorption where a reversal of Cotton Effect can be observed as the reaction proceeds. It seems fairly likely that both forms will eventually attain an equilibrium position.

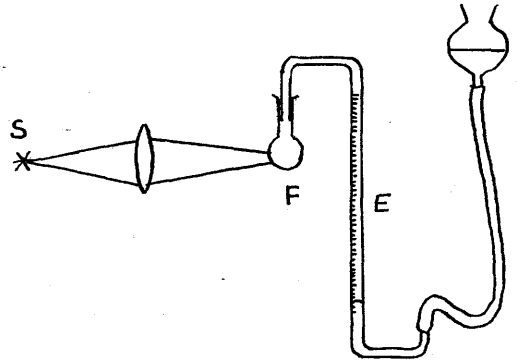
Although this is a very interesting phenomenon, it is an unfortunate complication from the asymmetric decomposition standpoint since the pure distereoisomer will give an equilibrium mixture before asymmetric decomposition will begin. This means that the initial rotatory power will be much less and more important opposite effects will result from the asymmetric decomposition of the two isomers now present. This will have a very deleterious effect on any rotation produced from the inactive material.

This result prompted a search for a terpene derivative which was more stable and free from the above defect. This was found in the pyridine salt of (+)-2-chloro-2-nitroso camphane-10-sulphonic acid described on page (56).

Photo-oxidation of (-)-2-chloro-2-nitroso-camphane.

This proceeded normally and gave a further proof of the identity of 2-chloro-2-nitroso camphane since it oxidised to 2-chloro-2-nitroso camphane which had already been characterised by Forster(62).

The apparatus is shown in sketch.



0.277 gms. 2-chloro-2-nitroso-camphane were dissolved in some oxygen free alcohol and this solution placed in the small flask F (capacity about 10 ml.). This was attached to the graduated tube E which was full of oxygen. After about 10 hours' illumination from a 60 watt lamp S, 16.5 ml. oxygen had been used and this volume did not change after a further 10 hours' irradiation. It is also of interest to note that no absorption of oxygen took place when the solution was kept in the dark.

Reduced to N.T.P. the volume of oxygen used was 15.57 ml. and calculation has shown that 0.2770 gms. 2-chloro-2-nitroso camphane requires 15.39 ml. oxygen for conversion to the nitro compound. The white solid extracted from the

alcohol at the end of the reaction had m.p. 217° and the analysis gave C = 54.86; H, 7.43; N = .

Forster gives m.p. 217° for 2-chloro-2-nitroso camphane and analysis calculated for $C_{10}H_{16}O_2NCl$ is C = 55.16; H = 7.35; N = 6.43.

ABSORPTION, CIRCULAR DICHROISM AND ROTATORY DISPERSION.

Absorption. All absorption measurements were taken using a "Unicam" photoelectric spectrophotometer.

The absorption spectrum of (-)-2-chloro-2-nitroso camphane is shown in Fig. (5), the experimental results being shown by the red line (Data shown in Table II). It will be seen that ε_{max} is 12.9 and λ_o is 6600 Å. There is a step out at 6100 Å due to a subsidiary band which is normal for the -NO group.

The experimental curve of Circular Dichroism has on analysis required three components so that it has also been necessary to postulate the existence of a third small component in the absorption band at 6925 Å, since circular dichroism cannot occur without absorption. The sum of the three components (green line in Fig. (5)) gives a fairly close agreement with the experimental curve (red line).

The three components required for the mathematical analysis are:-

(1) Large Component VI A. $\varepsilon_{max} = 11.27$ at $\lambda_o = 6600$ Å

(2) First Small Component VI B. $\varepsilon_{max} = 6.6$ at $\lambda_o = 6100$ Å

(3) Second Small Component VI C. $\varepsilon_{max} = 3.0$ at $\lambda_o = 6925$ Å.

Evidence for three components for the absorption of the-NO group is given in the case of NOCl by Goodeve and Katz[65], and Mitchell and Naismith also used three components

Fig. 5.

ABSORPTION of (-)2-Chloro-2-Nitrose Camphane.

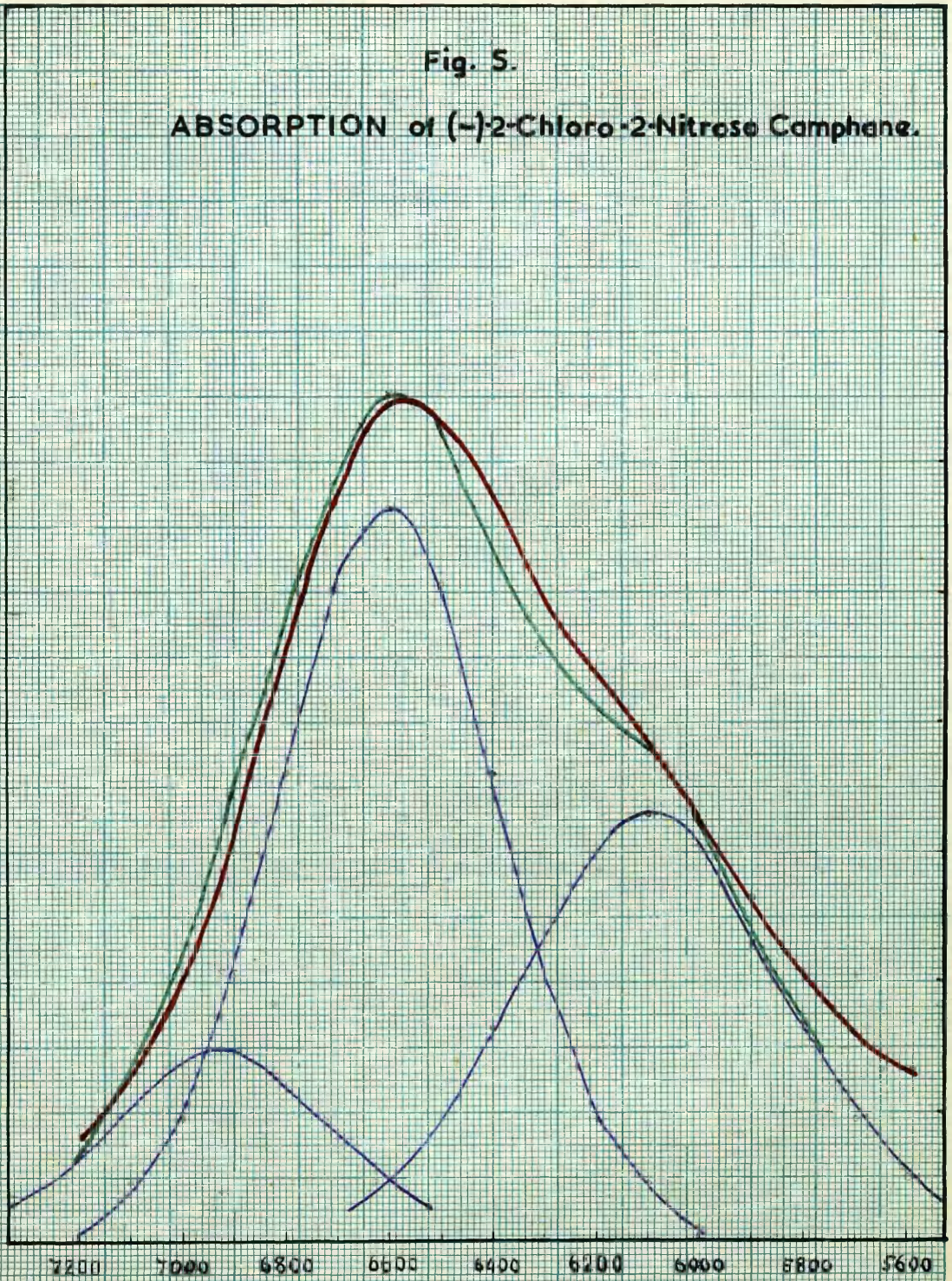


Table VI.

Analysis of Absorption Curves of (-)-2-chloro 2-nitroso Camphane.

(A) Large Component λ_o = 6600 ; ε_{max} = 11.27 ; θ = 300.

λ	ε
6600	11.27
6700 6500	10.07
6800 6400	7.22
6900 6300	4.14
7000 6200	1.90
7100 6100	0.93
7200 6000	0.20

(B) First Small Component. λ_o = 6100; ε_{max} = 6.6; θ = 360.

λ	ε
6100	6.6
6200 6000	6.1
6300 5900	4.62
6400 5800	3.30
6500 5700	1.92
6600 5600	0.99

Table VI (Contd.).

(C) Second Small Component. $\lambda_o = 6925$; $\varepsilon_{max} = 3.0$; $\theta = 300$.

λ	ε
6925	3.00
7025 6825	2.68
7125 6725	1.92
7225 6625	1.10
7325 6525	0.51

for the absorption curve of (-)- γ-chloro- γ-nitroso- δ-phenyl valeric acid[25].

Circular Dichroism. For the measurement of Circular Dichroism two methods have been employed.

The first is the method devised by Bruhat[14] in which ellipticities are measured and these are converted to Circular Dichroism using the equation

$$\left(\varepsilon_l \sim \varepsilon_r\right) = \frac{\varphi \times 0.0305}{cl.}$$

For this method the ordinary polarimeter was used as for rotation measurements - this consisted of a Hilger Polarimeter and a Zeiss Winkel Monochromator - but a $\lambda/4$ mica plate was inserted behind the Lippich polarising system. By adjustment of the $\lambda/4$ plate measurements of elliptical polarisation could be made. A full account of the adjustments required is given in Mitchell's "Cotton Effect and Related Phenomena" (p.44), London 1933.

A second method due to Dr. Mitchell is described later in this thesis under "Photoelectric measurement of Circular Dichroism" (p. 18) and consists essentially of a direct measurement of ε_l and ε_r. For this purpose the "Unicam" was employed having an attachment to produce the left-handed and right-handed circularly polarised light. The results for $(\varepsilon_l \sim \varepsilon_r)$ from both methods give good agreement but the direct method is the more accurate. (Fig. (6), Table (II)).

Fig. 6.

CIRCULAR DICHROISM of
(–)-2-Chloro-2-Nitroso Camphane.

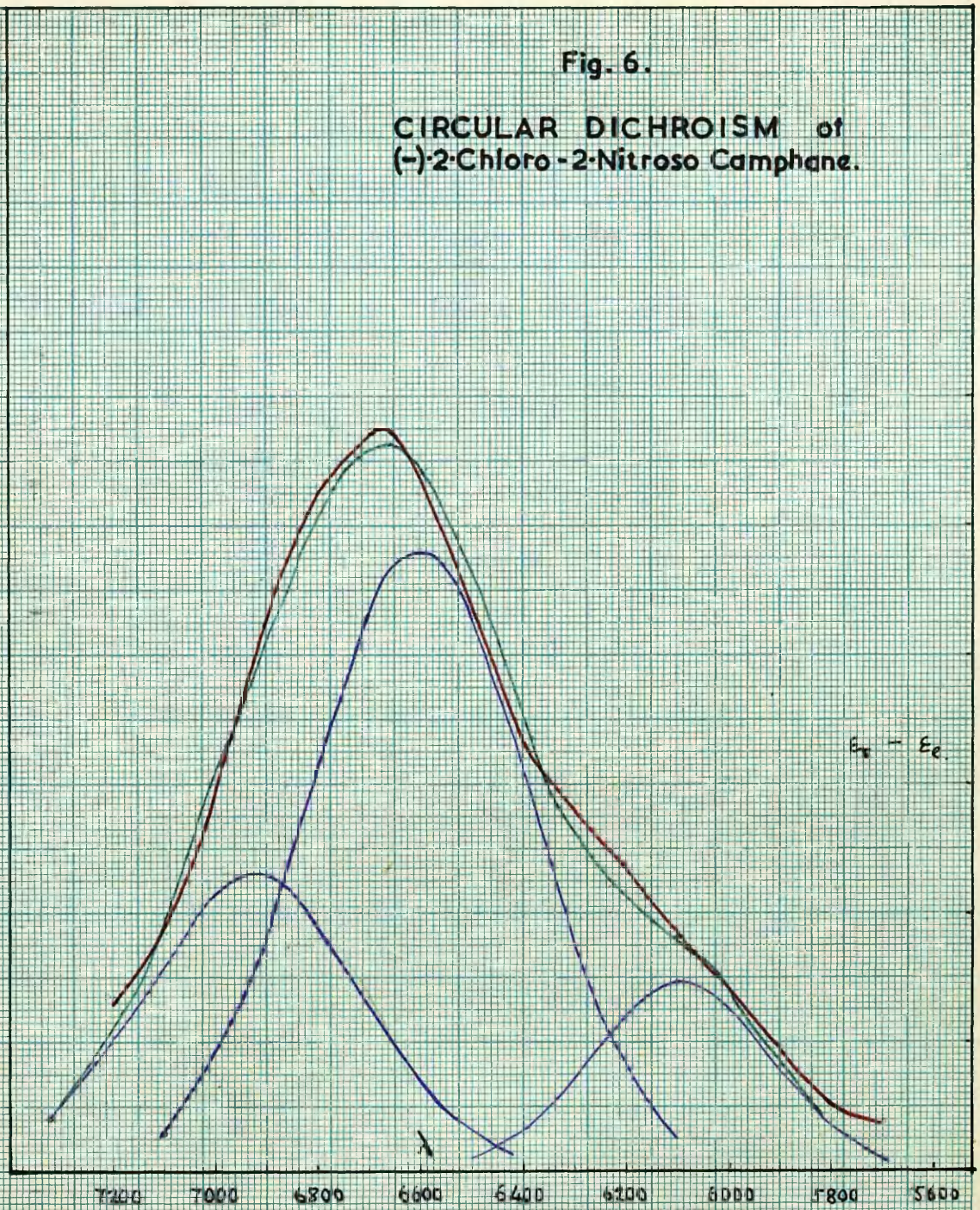


Table VII.

Analysis of Circular Dichroism Curves for

(-)-2-chloro 2-nitroso Camphane.

(A) Large Component. $\lambda_o = 6600$; $(\varepsilon_r - \varepsilon_\ell)_{max} = 0.96$; $\theta = 300$

λ	$(\varepsilon_r - \varepsilon_\ell)$
6600	0.96
6700 6500	0.86
6800 6400	0.66
6900 6300	0.35
7000 6200	0.16
7100 6100	0.06

(B) First Small Component. $\lambda_o = 6100$; $(\varepsilon_r - \varepsilon_\ell)_{max} = 0.29$; $\theta = 250$

λ	$(\varepsilon_r - \varepsilon_\ell)$
6100	0.29
6200 6000	0.25
6300 5900	0.15
6400 5800	0.07
6500 5700	0.02
6600 5600	0.004

Table VII (Contd.).

(C) Second Small Component. $\lambda_o = 6925$; $(\varepsilon_r - \varepsilon_e)_{max} = 0.46$; $\theta = 300.$

λ	$(\varepsilon_r - \varepsilon_e)$
6925	0.46
7025 6825	0.41
7125 6725	0.29
7225 6625	0.17
7325 6525	0.08
7425 6425	0.03.

A very striking point is that the maximum of Circular Dichroism (6700 Å) does not coincide with the maximum absorption (6600 Å). This means that the component absorption bands in (-)-2-chloro-2-nitroso camphane are not all equally active. As only active absorption bands contribute to Circular Dichroism, it is of interest to see how these results can be reconciled. Kuhn and Gore[66] observed a similar effect in camphor in which the circular dichroism was concentrated at the long wave side of the C=O band and was interpreted by these authors as an indication that the band consisted of two superimposed components, the long wavelength subsidiary band contributing practically the whole of the Circular Dichroism and the associated optical activity, whereas the short wave component was almost devoid of Circular Dichroism.

To see if the same effect was occurring here, a mathematical analysis of the Circular Dichroism and Absorption curves was made using the equations

$$\left(\varepsilon_\ell \sim \varepsilon_r\right) = \left(\varepsilon_\ell \sim \varepsilon_r\right)_{max} e^{-\left(\frac{\lambda-\lambda_0}{\theta}\right)^2} \qquad \text{---------- (18)}$$

and

$$\varepsilon = \varepsilon_{max}\, e^{-\left(\frac{\lambda-\lambda_0}{\theta}\right)^2} \qquad \text{---------- (15),}$$

and the curves produced by arbitrarily selecting values for $(\varepsilon_\ell \sim \varepsilon_r)$, ε and $\lambda - \lambda_0$ fitted together until the resultant curve closely resembled the experimental curve.

Kuhn and Gore postulated the existence of only two components to explain their results, but it was found in this case that three components were necessary to account for the discrepancy between ε_{max} and $(\varepsilon_r - \varepsilon_e)_{max}$. Figs. (5) and (6). Tables (VI) and (VII).

From the graphs it will be seen that the short wavelength absorption component at 6100 Å contributes very little to the Circular Dichroism but that the long wavelength component at 6925 Å although very small $\varepsilon_{max} = 3.0$, influences the circular dichroism to a large extent: the main component at 6600 Å has, of course, the greatest effect. These results are also borne out when considering the Anisotropy Factor 'g'.

Anisotropy Factor.

From the experimental values for Circular Dichroism and for Absorption it will be seen (Table II) that 'g' increases from 0.024 at 5800 to 0.150 at 7200. Results of a similar nature have been recorded for camphor and for camphor-10-sulphonic acid[66]. The high value of 'g' at 7200 would imply that there must be a very active absorption band in this region.

Comparison of the values of 'g' calculated from the component curves for $\lambda_o = 6100$ Å, $\lambda_o = 6600$ Å and $\lambda_o = 6925$ Å agree quite well with the experimental values.

λ	Theoretical	Experimental
6100 Å	0.044	0.047
6600 Å	0.085	0.084
6925 Å	0.150	0.137.

Rotatory Dispersion.

Measurements were taken visually using the polarimeter to which reference has already been made in connection with Circular Dichroism. The results are shown in Figs. (١) and (٢). The dip in the curve at about 6150 Å which does not occur in other chloro nitroso compounds has been fairly satisfactorily explained by the calculation of Rotatory Dispersion from the component Circular Dichroism curves and it will be seen here also that there is reasonable agreement between the observed and theoretical results. These substantiate the postulation of three absorption components since the resultant curve of Rotatory Dispersion is calculated from three component Circular Dichroism curves.

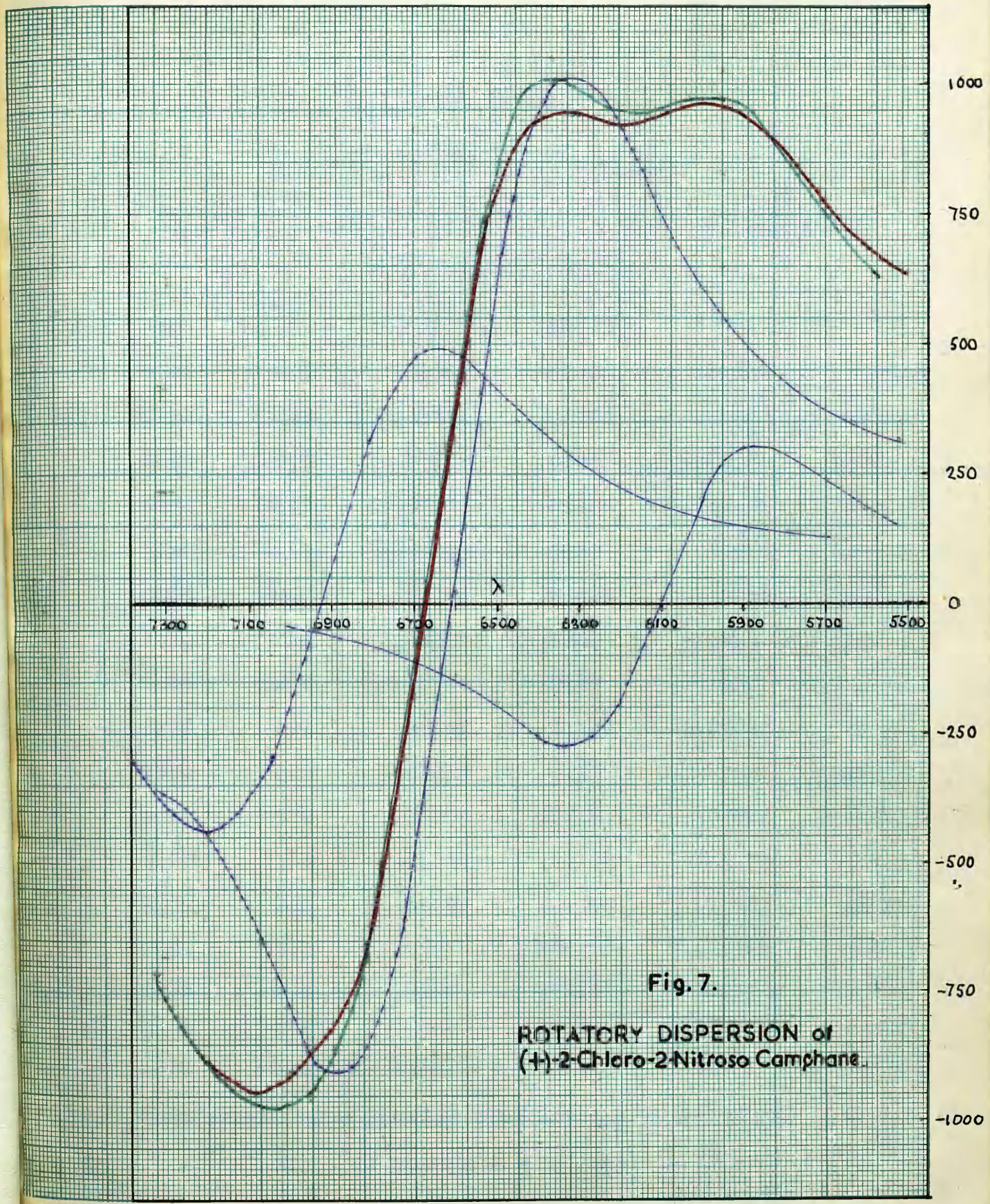


Fig. 7.

ROTATORY DISPERSION of
(+)-2-Chloro-2-Nitroso Camphane.

Table VIII.

(-)-2-chloro-2-nitroso Camphane.

Partial Rotations calculated from Large Component Curve of Circular Dichroism.

λ	c	$e^{-c^2}\int_0^c e^{x^2}dx.$	$\frac{\theta}{2(\lambda+\lambda_0)}$	m	$[\alpha]$
6600	0.0	.00000	.01136	.01136	20.15
6720	-0.4	-.35943	.01126	-.34683	-602.6
6840	-0.8	-.53210	.01121	-.52089	-891.0
6960	-1.2	-.50726	.01106	-.49620	-852.9
7080	-1.6	-.40000	.01096	-.38904	-643.0
7200	-2.0	-.30135	.01086	-.29049	-443.6
7320	-2.4	-.2353	.0107	-.2246	-359.1
7440	-2.8	-.1936	.0106	-.1830	-287.8
6480	0.4	.35943	.01147	+.37090	669.7
6360	0.8	.53210	.01157	.54367	1000.0
6240	1.2	.50726	.01163	.51889	973.1
6120	1.6	.40000	.01178	.41178	787.0
6000	2.0	.30135	.01190	.31325	610.8
5880	2.4	.2353	.01201	.24731	492.0
5760	2.8	.1936	.0121	.2057	417.8
5640	3.2*	.1563	.0122	.1685	349.5
5520	3.6*	.138	.0123	.1503	313

*For values of c greater than 3.2 the value of the integral $e^{-c^2}\int_0^c e^{x^2}dx.$ is approximately equal to $1/2c$.

Table IX.

(-)-2-chloro-2-nitroso Camphane.

Partial Rotations calculated from First Small Component Curve of Circular Dichroism.

λ	c	$e^{-c^2}\int_0^c e^{x^2}dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	m	$[\alpha]$
6100	0.0	.00000	.01024	.01024	3.5
6200	-0.4	-.35943	.01016	-.34927	-188.4
6300	-0.8	-.53210	.01008	-.52202	-264.5
6400	-1.2	-.50726	.01000	-.49726	-253.9
6500	-1.6	-.40000	.00992	-.39008	-191.4
6600	-2.0	-.30135	.00988	-.29147	-140.9
6700	-2.4	-.2353	.00976	-.2256	-110.0
6800	-2.8	-.1936	.00968	-.1840	- 88.4
6900	-3.2	-.1563	.00961	-.1467	- 69.47
7000	-3.6*	-.138	.00951	-.1295	- 46.67
6000	0.4	+.35943	.01033	.36976	201.2
5900	0.8	.53210	.01042	.54252	300.0
5800	1.2	.50725	.01051	.51777	271.8
5700	1.6	.40000	.01059	.41059	235.4
5600	2.0	.30135	.01069	.31204	182.1

Table X.

(-)-2-chloro-2-nitroso Camphane.

Partial Rotations calculated from Second Small Component Curve of Circular Dichroism.

λ	c	$e^{-c^2}\int_0^c e^{x^2}\,dx$.	$\frac{\theta}{2(\lambda+\lambda_0)}$	m	$[\alpha]$
6925	0.0	.0000	.01081	.01081	9.2
7045	-0.4	-.35943	,01075	-.34868	-291.9
7165	-0.8	-.53210	.01065	-.52145	-428.5
7285	-1.2	-.50726	.01055	-.49671	-402.4
7405	-1.6	-.40000	.01047	-.38953	-300.1
6805	0.4	.35943	.01095	.37038	321.0
6685	0.8	.53210	.01100	.54310	479.0
6565	1.2	.50726	.01112	.51838	466.0
6445	1.6	.40000	.01118	.41118	377.1
6325	2.0	.30135	.01134	.31269	291.6
6205	2.4	.2353	.01142	.24672	234.5
6085	2.8	.1936	.01153	.20513	198.2
5965	3.2	.15630*	.01163	.16793	162.2
5845	3.6	.138*	.01222	.15022	152.0
5725	4.0	.125*	.0125	.1375	133.4

Table XI.

(-)-2-chloro-2-nitroso Camphane.

Anisotropy Factor calculated from Component Curves of Circular Dichroism and Absorption.

(A) Large Curve

λ	ε	$(\varepsilon_r - \varepsilon_l)$	g.
6600	11.27	0.96	0.085
6700 6500	10.07	0.86	0.086
6800 6400	7.22	0.61	0.085
6900 6300	4.14	0.35	0.084
7000 6200	1.90	0.16	0.084

(B) First Small Component

λ	ε	$(\varepsilon_r - \varepsilon_l)$	g
6100	6.6	0.29	0.044
6200 6000	6.1	0.25	0.041
6300 5900	4.6	0.15	0.033
6400 5800	3.3	0.07	0.021
6500 5700	1.9	0.02	0.011

Table XI (Contd.).

(C) Second Small Component

λ	ε	$(\varepsilon_r - \varepsilon_e)$	q
6925	3.0	0.46	0.153
7025 6825	2.68	0.41	0.152
7125 6725	1.92	0.29	0.151
7225 6625	1.10	0.17	0.152
7325 6525	0.51	0.08	0.156

MATHEMATICAL REPRESENTATION OF ABSORPTION, CIRCULAR DICHROISM AND ROTATORY DISPERSION CURVES.

Circular Dichroism.

Simpson[67] employed the equation

$$(\varepsilon_\ell \sim \varepsilon_r) = (\varepsilon_\ell \sim \varepsilon_r)_{max} e^{-\left(\frac{\lambda - \lambda_o}{\theta}\right)^2} \qquad \text{------ (18)}$$

in order to analyse the practical Circular Dichroism curves for l-menthyl-d- β-chloro- β-nitroso butyrate and used two components in order to fit his experimental results. In order to do this the positions of the maxima of the two components and the wavelengths at which $(\varepsilon_\ell \sim \varepsilon_r)$ is half the maximum value were arbitrarily assumed, and, by trial and error, the best fit for the observed curve was obtained by summing the two components. In the present case three such components were required.

Large Component Curve.

Assume $\lambda_o = 6600$ where $(\varepsilon_r - \varepsilon_\ell)_{max} = 0.96$

and $\lambda = 6850$ where $(\varepsilon_r - \varepsilon_\ell) = 0.48$

i.e., $\lambda - \lambda_o = 250.$

From Equn. (18) $0.48 = 0.96\, e^{-\left(\frac{250}{\theta}\right)^2}$

thus $\theta = 300.$

Substituting again in (18) we have

$$\log. x = \log. 0.96 - \left(\frac{D}{300}\right)^2 .4343$$

where D is the difference in the wavelength between the maximum and a point on the curve where the Circular Dichroism

has the value x. By giving D values 100, 200, 300, 400, 500, etc., x was calculated; the values are shown in Table (VIIA) and graphed in Fig. (6).

Similar treatment was required for the other components which are:-

First Small Component - Table VIIB.

$\lambda_0 = 6100$ where $(\varepsilon_r - \varepsilon_e)_{max} = 0.29$

$\lambda = 6300$ where $(\varepsilon_r - \varepsilon_e) = 0.145$

i.e., $\lambda - \lambda_0 = 200$ and $\theta = 250$.

Second Small Component - VII C.

$\lambda_0 = 6925$ where $(\varepsilon_r - \varepsilon_e)_{max} = 0.46$

$\lambda = 7175$ where $(\varepsilon_r - \varepsilon_e) = 0.23$

i.e., $\lambda - \lambda_0 = 250$ and $\theta = 300$.

The sum of these three curves agrees fairly well with the experimental curve.

Absorption.

In the same way the absorption curves were assumed to consist of thee components of the type

$$\varepsilon = \varepsilon_{max}\, e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \qquad \text{----- (15)}$$

Large Component - VI A.

$\lambda_0 = 6600$ $\varepsilon_{max} = 11.27$

$\lambda = 6850$ $\varepsilon = 5.63$

i.e., $\lambda - \lambda_0 = 250$ and $\theta = 300$.

First Small Component - VI B.

$\lambda_o = 6100$ $\quad \varepsilon_{max} = 6.6$

$\lambda = 6400$ $\quad \varepsilon = 3.3$

i.e., $\lambda - \lambda_o = 300$ and $\theta = 360.$

Second Small Component - VI C.

$\lambda_o = 6925$ $\quad \varepsilon_{max} = 3.0$

$\lambda = 7175$ $\quad \varepsilon = 1.5$

i.e., $\lambda - \lambda_o = 250$ and $\theta = 300.$

ROTATORY DISPERSION. CALCULATIONS OF PARTIAL ROTATIONS DUE TO THE NITROSO GROUP.

The contributions to the Rotatory Dispersion associated with each of the component Circular Dichroism curves were calculated by means of Lowry and Hudson's equation referred to in the Introduction. Details of the procedure are given in Lowry, "Optical Rotatory Power", p.450.

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{(\varepsilon_\ell \sim \varepsilon_r)_{max}}{\log_{10} e} \frac{\lambda_o}{\lambda} \left[e^{-\left(\frac{\lambda-\lambda_o}{\theta}\right)} \int_o^{\left(\frac{\lambda-\lambda_o}{\theta}\right)^2} e^{x^2} dx + \frac{\theta}{2(\lambda+\lambda_o)} \right] \quad \text{--- (A)}$$

Converting this equation to degrees and letting 'm' represent the terms inside the bracket we obtain

$$[M] = \frac{100}{2\sqrt{\pi}} \cdot \frac{57.296}{.4343} \cdot (\varepsilon_\ell \sim \varepsilon_r)_{max} \cdot \frac{\lambda_o}{\lambda} \cdot m$$

$$\therefore [M] = 3723. (\varepsilon_\ell \sim \varepsilon_r)_{max} \cdot \frac{\lambda_o}{\lambda} \cdot m$$

$$[\alpha] = \frac{3723 \cdot 100}{M} \cdot (\varepsilon_\ell \sim \varepsilon_r)_{max} \cdot \frac{\lambda_o}{\lambda} \cdot m \quad \text{--- (B)}$$

where M is the molecular weight of the compound - in this case 201.5.

Application to large Component of Circular Dichroism - XIII.

Here $(\varepsilon_r - \varepsilon_\ell) = 0.96$ occurs at $\lambda_o = 6600$ Å. $\theta = 300$. These values inserted are in equation (B) -

$$[\alpha] = \frac{3273 \cdot 100}{201.5} \cdot 0.96 \cdot 6600 \cdot \frac{m}{\lambda} \quad \text{--- (C)}$$

To obtain the value of 'm' (i.e., the value of the terms inside the large brackets in equation A) corresponding

to λ the procedure is as follows:

Six columns are headed as in Table VIII. In column (2) are tabulated the values of 'c' for which the corresponding integral is known. These values are in column (3).

Now since $c = \frac{\lambda + \lambda_0}{\theta}$ $\therefore$ $\lambda = \lambda_0 + c.\theta$

but $\theta = 300$ $\therefore$ $\lambda = \lambda_0 + c.300$

Thus for an increment of 0.1 in the value of c there is an interval in wavelength of 30 Å. By addition or subtraction from λ_0 the wavelengths corresponding to different values of c are calculated in column (1).

Column (4) contains the values of $\frac{\theta}{2(\lambda + \lambda_0)}$ and by summing columns (3) and (4), column (5) is obtained. The series of values for m and λ now obtained can be substituted in equation C to give the desired rotations (column (5)).

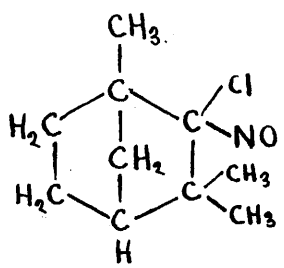
Similar results are shown for the First Small Component Curve in Table IX and for the Second Small Component Curve in Table X.

The summation of all three curves is shown by the green line in Fig. 7 and it agrees fairly well with the experimental curve (red line).

OTHER CHLORO NITROSO TERPENES.

When (-)-2-chloro-2-nitroso camphane was first prepared it was found that the Cotton Effect was small, so that it was thought advisable to study other terpene derivatives. The first of these was the compound corresponding to fenchone.

(+)-2-chloro-2-nitroso Fenchane (VII) was made from fenchone oxime in a similar way to that for 2-chloro-2-nitroso camphane. It is a blue solid, m.p. 90-95°, but much less stable than the corresponding camphor compound. Unlike the blue camphane, no increase in rotation was observed when the hydrochloride of the oxime was used in place of the oxime. This is probably due to the fact that the oxime itself is rather insoluble in ether.



VII

Rotatory Dispersion and Absorption Curves are shown in Fig. data in Table XII. The rotatory dispersion is in the opposite sense to that of (-)-2-chloro-2-nitroso camphane and shows maximum at $[\alpha]_{7000} = +250^{\circ}$, while the minimum is at $[\alpha]_{6100} = -400^{\circ}$. The absorption maximum is slightly higher, being $\varepsilon_{max} = 16.5$ at $\lambda = 6700$ Å.

These results for rotatory dispersion are much lower than for the corresponding camphor compound and are probably due in part to the activity of the fenchone used which was $[\alpha]_D = +46^\circ$. The literature gives the figure $+63^\circ$, while one author (Huckel) gives it at $[\alpha]_D +75^\circ$ [68]. A sample of commercial fenchone had $[\alpha]_D = +10.8^\circ$.

Photochemical Action of Red Light.

Under the influence of red light the blue fenchane behaved in much the same way as the blue camphane, curves similar to those of Fig. 2. being obtained. In this case, however, there was also a dark reaction since it was noted that once the reaction had been initiated, it proceeded, more slowly it is true, when the light was absent.

This effect, coupled with the fact that only a small quantity of fenchone was available, made 2-chloro-2-nitroso fenchane rather unsuitable for the present work.

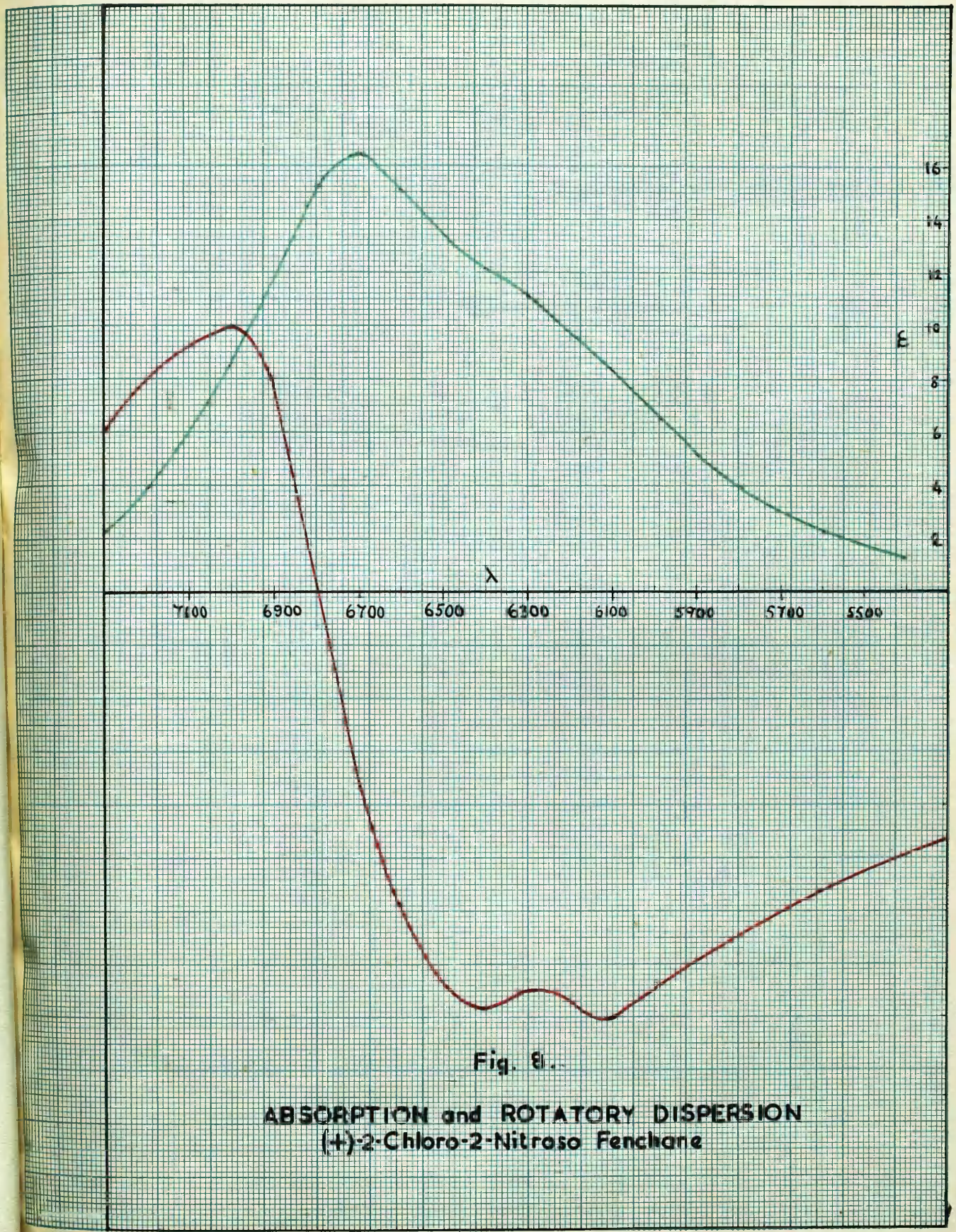


Fig. 8.

ABSORPTION and ROTATORY DISPERSION
(+)-2-Chloro-2-Nitroso Fenchane

Table XII

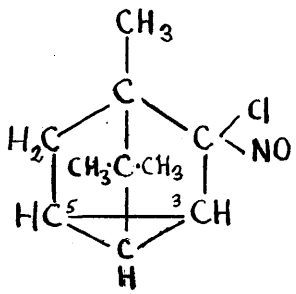
Rotatory Dispersion and Absorption of (+)-2-chloro-2-nitroso Fenchane.

For [α] concn. = 0.186 gms./100 ml. Ethanol. l = 1 dm.

For ε concn. = 0.061 M. in Ethanol. l = 1 cm.

λ	α	[α]	ε
4500	-.27	-145°	--
4700	-.28	-150°	--
5000	-.34	-183°	--
5200	-.40	-215°	--
5400	-.46	-245°	1.6
5600	-.52	-280°	2.2
5800	-.63	-340°	4.0
5900	-.64	-345°	5.1
6000	-.69	-370°	6.45
6100	-.74	-400°	8.4
6200	-.71	-380°	9.5
6300	-.68	-365°	11.1
6400	-.72	-390°	12.0
6500	-.68	-365°	14.3
6600	-.55	-295°	15
6700	-.34	-183°	16.5
6800	+.03	+16°	15
6900	+.37	+200°	11
7000	+.47	+250°	8.5
7100	+.43	+231°	--
7200	+.38	+201°	4.0
7300	+.28	+150°	1.6

(-)-2-chloro-2-nitroso Isocyclene (VIII).



VIII

Isocychenone* or dehydrocamphor $[\alpha]_D$ = +61.5° in ethanol was fairly easily made from camphor(69) and it was hoped that the bridge between carbons 3 and 5 might have an inhibiting effect on the so-called photomutarotation produced by red light. The blue solid, m.p. 130° was produced in the normal way from the oxime hydrochloride and in this case exactly similar results were obtained as with camphoroxime, the oxime hydrochloride giving a Rotatory Dispersion of greater magnitude than that when the oxime itself was used.

Rotatory Dispersion and Absorption Curves are shown in Fig. (Table XIII). The Rotatory Dispersion Curve is in the same sense as that of (+)-2-chloro-2-nitroso camphane, but shows a larger dip at about 6200 Å and the curve is also not symmetrical. It is possible that a chromatogram would have improved the rotation but the blue compound was not obtainable in large enough quantities to try this. Figures for maximum and minimum rotations were: $[\alpha]_{6000}$ = +178°, $[\alpha]_{6900}$ = -600°. Absorption ε_{max} = 15.0 at 6600. The maximum Extinction Coefficient is thus also higher than for the corresponding camphor compound.

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* See Footnote on p.70.

Photochemical Action of Red Light.

The action of red light is exactly analogous to that produced when (-)-2-chloro-2-nitroso camphane was similarly illuminated. The rotations at 6000 Å changed quickly from a positive to a negative value, reaching an equilibrium before other decomposition set in. There is no dark reaction, it is true, but the substance has no advantages over 2-chloro-2-nitroso camphane and it is somewhat tedious to prepare.

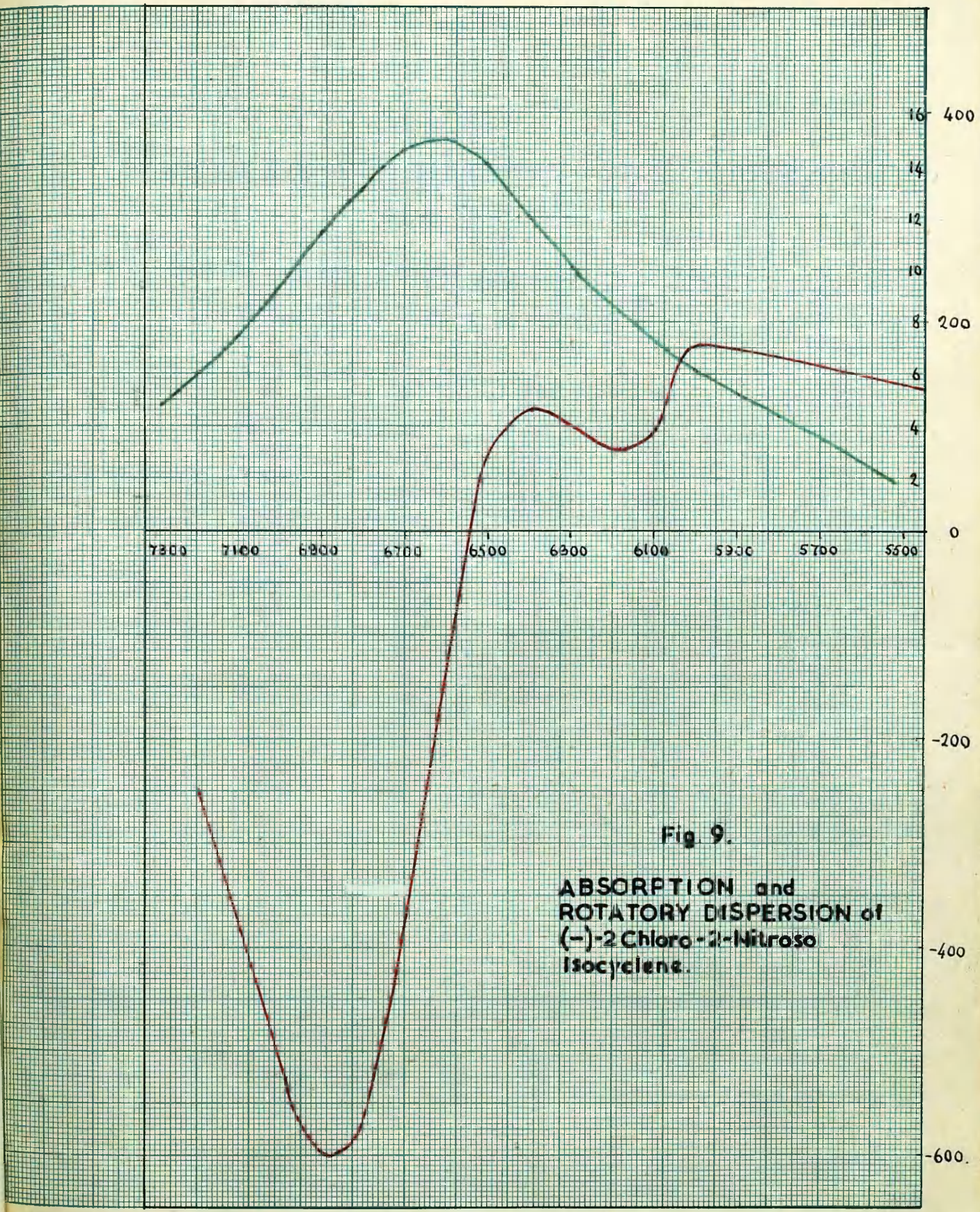


Fig. 9.

ABSORPTION and ROTATORY DISPERSION of (−)-2 Chloro-2-Nitroso Isocyclene.

Table XIII.

Rotatory Dispersion and Absorption of (−)-2-chloro-2-nitroso Isocyclene.

For [α] concn. = 0.218 gms./100 ml. Ethanol. l = 1 dm.

For ε concn. = 0.05 M in Ethanol l = 1 cm.

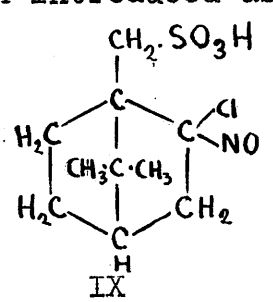
λ	α	[α]	ε
5000	+.21°	+ 97°	-
5500	+.30°	+140°	1
5800	+.36°	+168°	4.3
5900	+.37°	+172°	5.2
6000	+.38°	+178°	6.1
6100	+.20°	+ 93°	7.0
6200	+.15	+ 70°	8.3
6300	+.20°	+ 93°	10
6400	+.25°	+116°	12
6500	+.15°	+ 70°	14
6600	-.25°	-116°	15
6700	-.80°	-370°	14.5
6800	-1.25°	-573°	13
6900	-1.30°	-600°	10.7
7000	-1.00°	-475°	9
7100	-0.8°	-370°	7.4
7200	-0.5°	-247°	6

PHOTOCHEMISTRY OF THE PYRIDINE SALT OF (-)-2-CHLORO-2-NITROSO CAMPHANE-10-SULPHONIC ACID.

The chloro-nitroso terpenes described in the preceding section although displaying good Cotton Effects in the visible region, show a reversal in sign of rotation under the influence of red light and this renders them unsuitable for asymmetric photolysis.

The preparation of (-)-2-chloro-2-nitroso camphane-10-sulphonic acid was embarked upon for two reasons. Firstly, it was hoped that the introduction of the sulphonic group might stabilise the molecule against the "photo-mutarotation" effect, and secondly, by analogy with the bornylamine and neobornylamine hydrochlorides it was thought that salt formation (the pyridine salt was used) might effect a separation between the distereoisomers if they indeed existed.

It is important to note that the sulphonic group is in the 10 position and that no other asymmetric centre has been introduced as a complication. The position of the sulphonic group was obscure for some time, but there seems little doubt that it is in the 10 position and not in the 6[70].



IX

Preparation of the pyridine salt of (-)-2-chloro-2-nitroso camphane-10-sulphonic acid. Camphor was first converted

into camphor-10-sulphonic acid - Reychler's acid - and then into the oxime $[\alpha]_D = -113^\circ$ in methanol[71]. For the preparation of the chloro-nitroso compound a different procedure had to be adopted from that used for 2-chloro-2-nitroso camphane, as the free acid could not be made directly in the normal manner. The acid oxime was only very slightly soluble in ether and the solution did not become blue on the addition of chlorine. Dissolved in hydrochloric acid and chlorine added had again no effect. The oxime did not appear to form a hydrochloride. When dissolved in pyridine, however, a green colour was produced immediately, but the temperature had to be kept at -10° for best results. The blue substance produced by this method was found to be the pyridine salt and not the free acid. It was, however, a beautifully blue crystalline substance and very easily purified by crystallisation from ethanol. The free acid could be obtained by acidification of the salt with concentrated hydrochloric acid, but it was much more unstable and could not be easily crystallised, so that for all measurements of absorption, circular dichroism and rotatory dispersion, the pyridine salt was employed although in the case of the Asymmetric photolysis the free acid was used.

The pyridine salt of (-)-2-chloro-2-nitroso camphane-10-sulphonic acid has the following characteristics:-

Table XIV.

Rotatory Dispersion of the Pyridine Salt of (+)-2-chloro-2-nitroso camphane-10-sulphonic acid in Methyl Alcohol.

c = 0.220 g./100 ml. ; l = 1 dm. ; t = 18°.

λ	α	$[\alpha]$
4750	-0.65	-295
5000	-0.76	-345
5200	-0.96	-436
5400	-1.20	-546
5500	-1.35	-614
5600	-1.40	-636
5700	-1.35	-614
5800	-1.15	-523
5900	-1.00	-455
6000	-0.90	-409
6100	-0.58	-264
6200	-0.20	- 91
6300	+0.85	+386
6400	+1.50	+682
6500	+1.75	+795
6550	+1.77	+805
6600	+1.70	+773
6800	+1.20	+546
6900	+0.95	+432
7000	+0.80	+364
7200	+0.60	+273.

Table XV.

Circular Dichroism and Absorption of the Pyridine Salt of (+)-2-chloro-2-nitroso camphane-10-sulphonic acid in Methyl Alcohol.

For $(\varepsilon_\ell - \varepsilon_r)$ concn. = 0.0151 M ; l = 2.5 cm.,
and for ε concn. = 0.0230 M ; l = 1 cm.

λ	$(\varepsilon_\ell - \varepsilon_r)$	ε	g
5200	0.08	2.30	0.035
5400	0.15	3.90	0.038
5500	0.21	5.10	0.041
5600	0.30	6.70	0.045
5700	0.49	9.20	0.053
5800	0.64	10.80	0.059
5900	0.70	11.80	0.059
6000	0.86	13.80	0.062
6100	1.05	16.20	0.065
6200	1.14	17.80	0.064
6150	1.21	18.50	0.065
6250	1.27	19.20	0.066
6300	1.21	19.40	0.062
6350	1.14	18.80	0.061
6400	1.05	17.30	0.061
6500	0.71	12.80	0.055
6600	0.49	8.30	0.059
6700	0.26	5.20	0.050
6800	0.08	3.30	0.024
6900	0.04	2.00	0.020

$[\alpha]_{6650} = +805^{\circ}$ $[\alpha]_{5600} = -630^{\circ}$ $[\alpha]_{6250} = 0.0^{\circ}$

$\varepsilon_{max} = 19.4$ at $\lambda_{\circ} = 6250$

$(\varepsilon_{\ell} - \varepsilon_{r})_{max} = 1.27$ at $\lambda = 6250$

$g = 0.066$ at 6250Å

m.p. = 155°

Analysis: Found, C = 49.86; H = 5.77; N = 7.87%

Calculated for $C_{15}H_{21}O_4N_2ClS$ requires

C = 49.93; H = 5.82; N = 7.77%.

The compound prepared as above immediately gave a good Cotton Effect. Fractional crystallisation increased the melting point from 153° to 155° after six recrystallisations and also increased the rotatory power slightly. Nevertheless, it does not seem likely that a separation of isomers was taking place, rather is the process one of purification. It may be that the second isomer exists as in the case of 2-chloro-2-nitroso camphane, but evidence of this has not yet been obtained.

Absorption, Circular Dichroism and Rotatory Dispersion.

Absorption (Table XV) (Fig. 10). The introduction of the sulphonic group appears to have had two effects on the absorption. Firstly, that ε_{max} has been increased to 19.4 from 12.9 for 2-chloro-2-nitroso camphane: secondly, that the head of the absorption band has been displaced by nearly

Fig. 10.

ABSORPTION of Pyridine Salt of
(+)-2-Chloro-2-Nitroso Camphane-10-Sulphonic Acid.

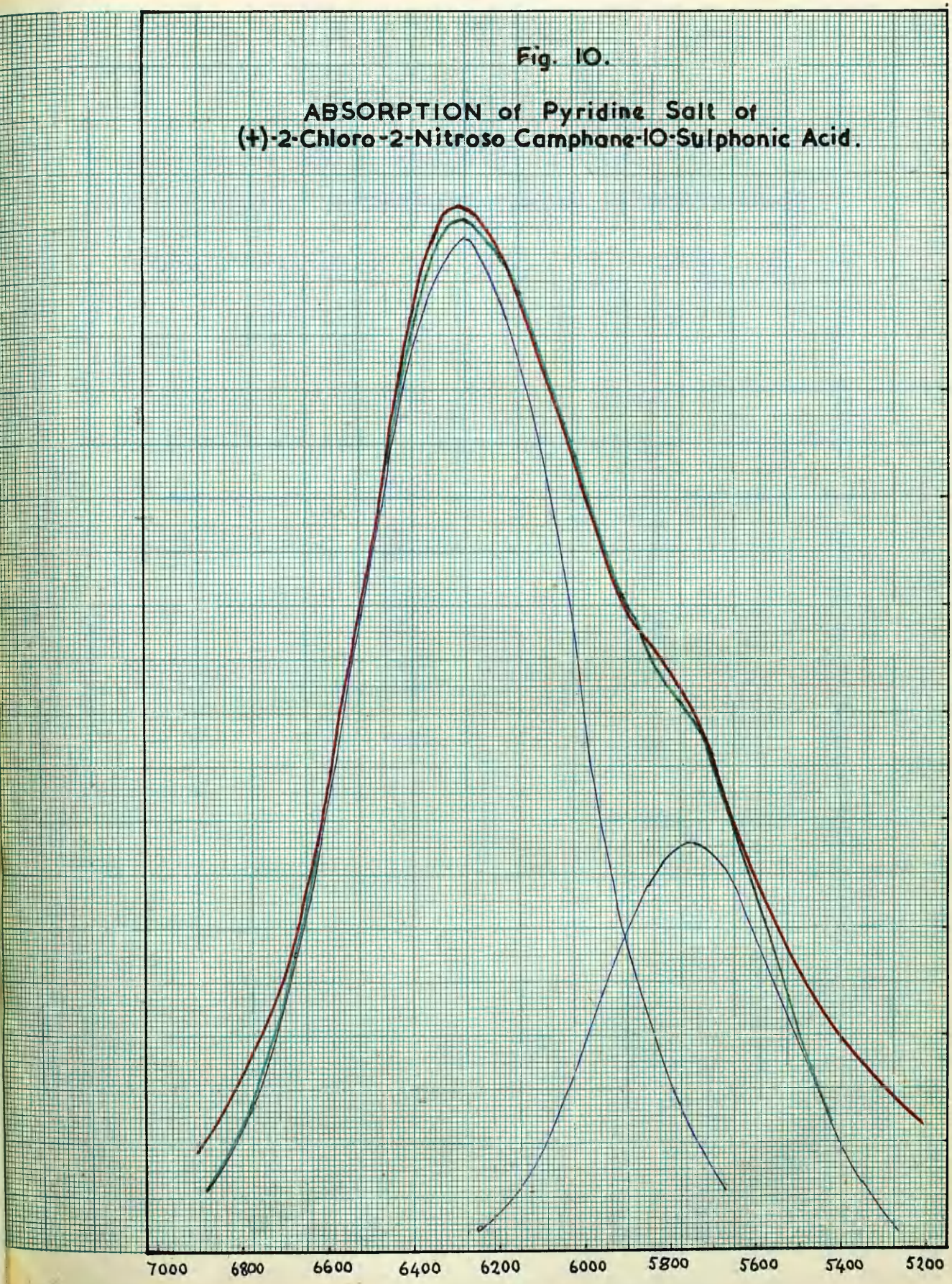


Table XVI.

Analysis of absorption curves of Pyridine Salt of (+)-2-chloro 2-nitroso camphane 10 sulphonic acid.

Larger Component. $\lambda_o = 6275$; $\epsilon_{max} = 18.8$; $\theta = 360$

λ	ϵ
6275	18.8
6375 6175	17.41
6474 6075	13.81
6575 5975	9.39
6675 5875	5.47
6775 5775	2.73
6875 5675	1.17
6975 5575	0.42

Table XVI (Contd.).

Smaller Component. $\lambda_0 = 5750$; $\varepsilon_{max} = 7.6$; $\theta = 300$

λ	ε
5750	7.6
5850 5650	6.80
5950 5550	4.87
6050 5450	2.79
6150 5350	1.28
6250 5150	0.47

Fig. II.

CIRCULAR DICHROISM of Pyridine Salt of
(+)-2-Chloro-2-Nitroso Camphane-10-Sulphonic Acid.

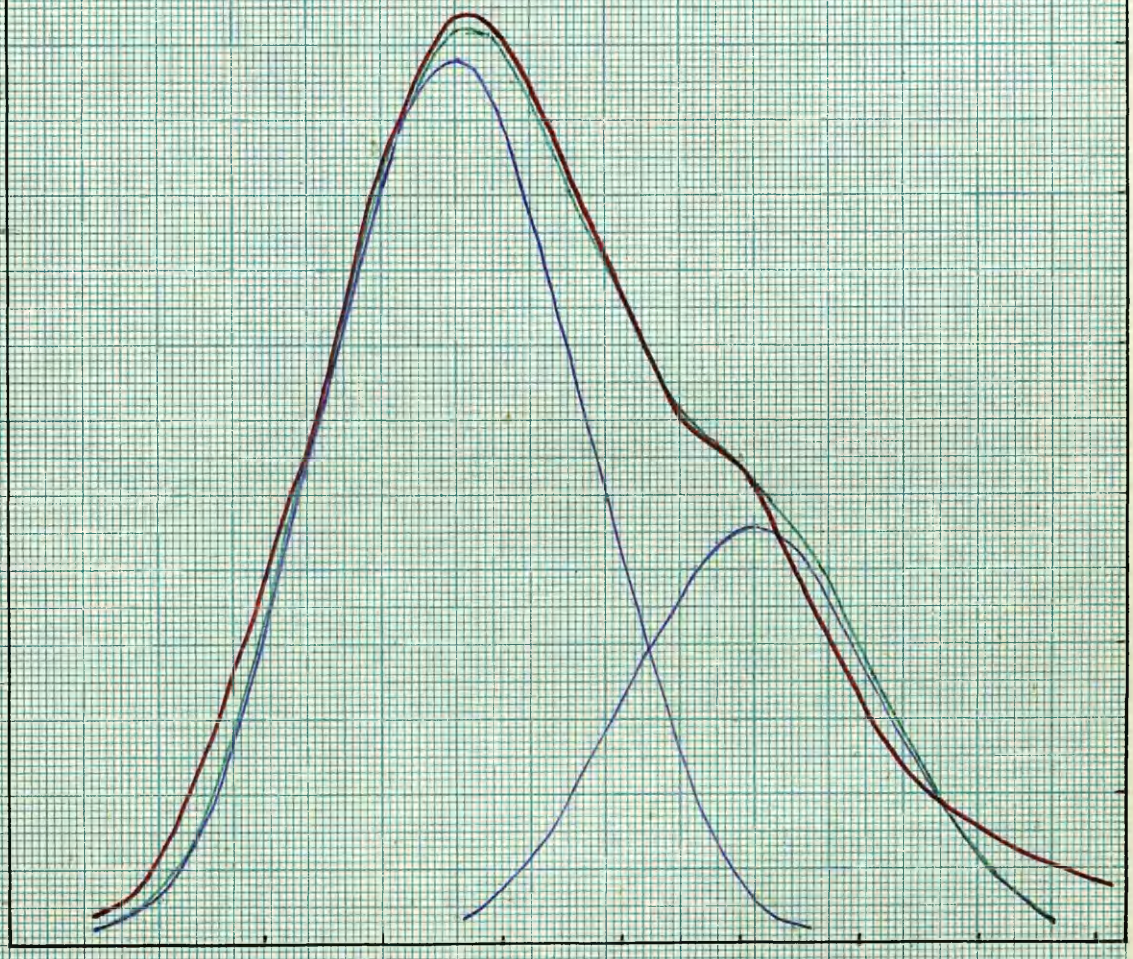


Table XVII.

Analysis of Circular Dichroism curves for Pyridine Salt of (+)-2-chloro 2-nitroso camphane 10 sulphonic acid.

Larger Component. $\lambda_o = 6275$; $(\varepsilon_l - \varepsilon_r)_{max} = 1.18$ m; $\theta = 300$.

λ	$(\varepsilon_l - \varepsilon_r)$
6275	1.18
6375 6175	1.06
6475 6075	0.75
6575 5975	0.46
6675 5875	0.20
6775 5775	0.058
6875 5675	0.021

Table XVII (Contd.).

Smaller Component $\lambda_o = 5775$; $(\varepsilon_e - \varepsilon_r)_{max} = 0.56$; $\theta = 300$

λ	ε
5775	0.56
5875 5675	0.50
5975 5575	0.36
6075 5475	0.20
6175 5375	0.095
6275 5275	0.035

Fig. 12.

ROTATORY DISPERSION of Pyridine Salt of (+)2-Chloro-2-Nitroso Camphane-10-Sulphonic Acid.

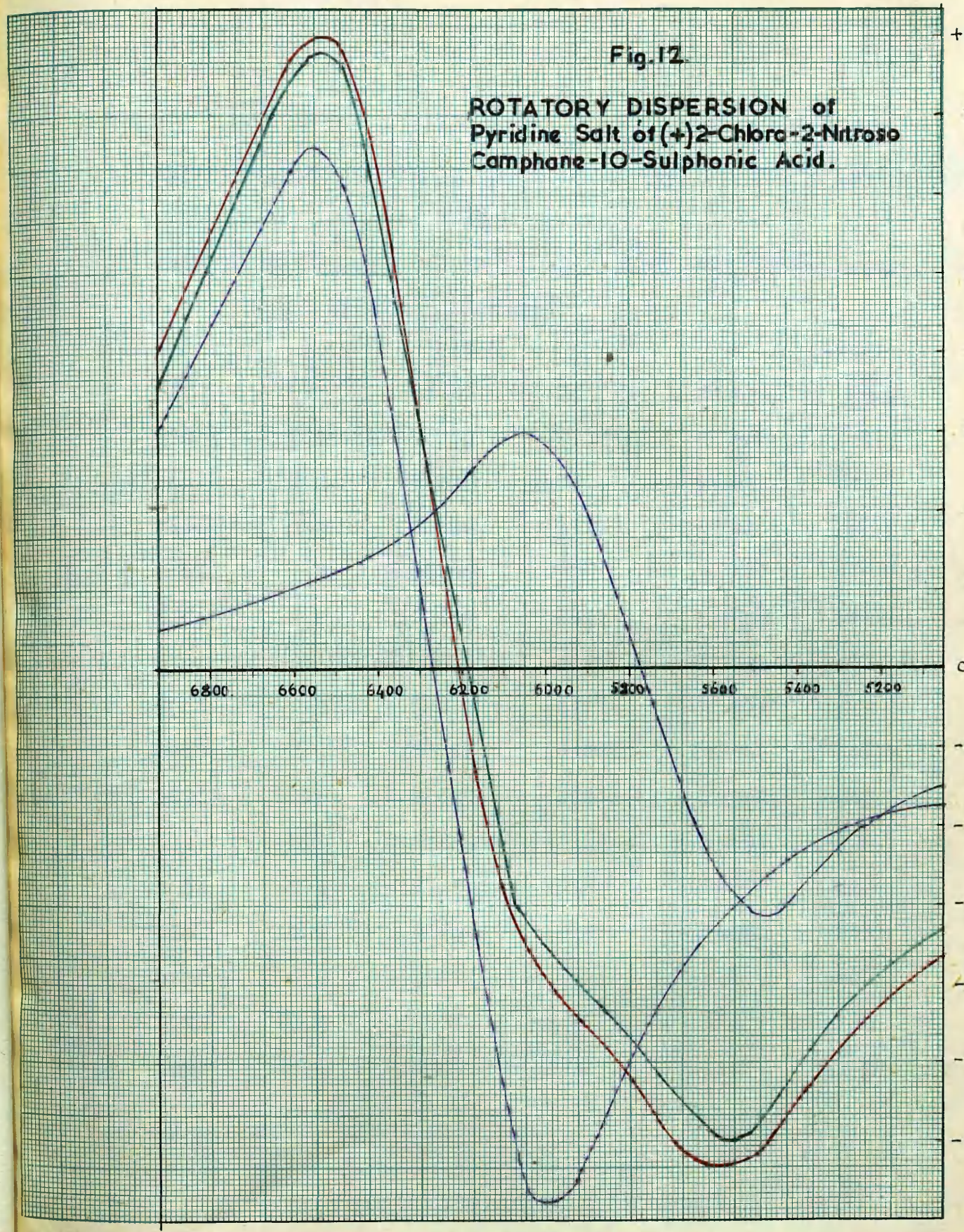


Table XVIII.

Pyridine Salt of (+)-2-chloro 2-nitroso camphane 10 sulphonic acid.

Partial Rotations calculated from large component curve of Circular Dichroism.

λ	c	$e^{-c^2}\int_0^c e^{x^2}dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	m	$[\alpha]$
6275	0.0	.00000	.01191	.01191	14.5
6395	0.4	.35943	.01182	.37125	445.2
6515	0.8	.53210	.01169	.54379	640.0
6635	1.2	.50726	.01157	.51883	600.0
6755	1.6	.40000	.01149	.41149	467.7
6875	2.0	.30135	.01140	.31275	345.0
6155	-0.4	-.35943	.01200	-.34725	-432.0
6035	-0.8	-.53210	.01214	-.51996	-660.9
5915	-1.2	-.50726	.01231	-.49495	-643.7
5795	-1.6	-.40000	.01238	-.38762	-513.7
5675	-2.0	-.30135	.0124	-.28895	-390
5555	-2.4	-.23530	.0126	-.22273	-302
5435	-2.8	-.19360	.0127	-.18093	-255
5315	-3.2	-.15630	.0130	-.1433	-206
5195	-3.6	-.138*	.013	-.125	-188
5075	-4.0	-.125*	.013	-.112	-172

Table XIX.

Pyridine Salt of (+)-2-chloro 2-nitroso camphane-10-sulphonic acid.

Partial Rotations calculated from small component of Circular Dichroism.

λ	c	$e^{-c^2}\int_0^c e^{x^2}\,dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	m	[α]
5775	0.0	.00000	.01292	.01292	6.3
5895	0.4	.35943	.01280	.37223	202
6015	0.8	.53210	.01265	.54448	291
6135	1.2	.50726	.01254	.51980	272
6255	1.6	.40000	.01242	.41242	213
6375	2.0	.30135	.01229	.31464	159
6495	2.4	.23530	.01219	.24749	130
6615	2.8	.19360	.01206	.20566	102
6735	3.2	.15630	.01194	.16824	80.5
6855	3.6*	.1389	.01190	.1408	53.0
5655	-0.4	-.35943	.01307	-.34636	-203
5535	-0.8	-.53210	.01320	-.51890	-300
5415	-1.2	-.50726	.01335	-.49491	-294
5295	-1.6	-.40000	.01349	-.38651	-235
5175	-2.0	-.30135	.01355	-.28790	-179
5055	-2.4	-.2353	.0137	-.2213	-137

300 Å to 6250 Å. This is rather unusual and seems to be the lowest wavelength recorded for a nitroso compound. The nearest example hitherto described is absorption of l-menthyl-d-β-chloro-β-nitroso butyrate described by Mitchell and Simpson[24] where $\varepsilon_{max} = 18$ at $\lambda = 6350$ Å.

The form of the curve is also very similar to that of the above compound, and mathematical analysis has shown the presence of two components. These occur at $\varepsilon_{max} = 18.8$ at $\lambda_o = 6275$ and $\varepsilon_{max} = 7.6$ at $\lambda_o = 5750$. Data for the theoretical components are given in Table XV and their sum (Fig. 10) agrees fairly well with the experimental curve.

Circular Dichroism. In contrast with (-)-2-chloro-2-nitroso camphane where the maxima of $(\varepsilon_e - \varepsilon_r)$ and ε do not coincide, the maxima for both the absorption and circular dichroism are very close indeed to 6250 Å. This made analysis much easier and the curve has also been analysed into two components. (Tables XVII and XVI). These maxima are at $\lambda_o = 6275$ where $(\varepsilon_e - \varepsilon_r)_{max} = 1.18$, and $\lambda_o = 5775$ where $(\varepsilon_e - \varepsilon_r)_{max} = 0.56$.

Anisotropy Factor. Also in contrast with (-)-2-chloro-2-nitroso camphane where 'g' increases with increasing wavelength, it will be seen from Table XV that 'g' rises to a maximum of 0.066 in the centre of the band and remains fairly stationary. From the analysis of the two curves

of absorption and circular dichroism it will be seen that each contributes about the same towards the rotatory dispersion since 'g' in each band is about 0.07.

For a comparison of the Absorption, Circular Dichroism and Anisotropy Factor of the pyridine salt of (2)-chloro-2-nitroso camphane-10-sulphonic acid with those of (-)-2-chloro-2-nitroso camphane it is of interest to consult Fig. 13 and 14.

Rotatory Dispersion (Table XIV) (Fig. 12.). The rotatory dispersion curve is the reverse of that for the blue camphane and shows a more normal dispersion than that for the terpene compounds, having no subsidiary dip but merely a slight step out at 5800 Å. The position of zero rotation is at 6250 Å and this also coincides with the maximum of absorption and Circular Dichroism.

Mathematical Analysis of the Rotatory Dispersion Curves in an analogous manner to that employed for 2-chloro-2-nitroso camphane for circular dichroism curves has again produced components whose sum agrees well with the experimental curves. (See Tables XVIII and XIX, and Fig. 12.).

Asymmetric Photolysis of (2)-chloro-2-nitroso camphane-10-sulphonic acid.

In order to determine whether or not the sulphonic acid would behave in the same way as 2-chloro-2-nitroso

camphane a similar experiment was tried using the active blue acid and exposing it to red light. However, in this case it was evident that no "photo-mutarotation" was occurring as the rotation altered only very slowly and, as it altered, so also did the absorption of the solution decrease. Several days' illumination were required before the colour was completely discharged. At no time during this period did the rotation reverse its sign.

A 10% solution of the active blue salt was found to give a readable rotation in a 1 dm. tube of -25° at 5000 Å, so that by using this figure in Kuhn's Equation

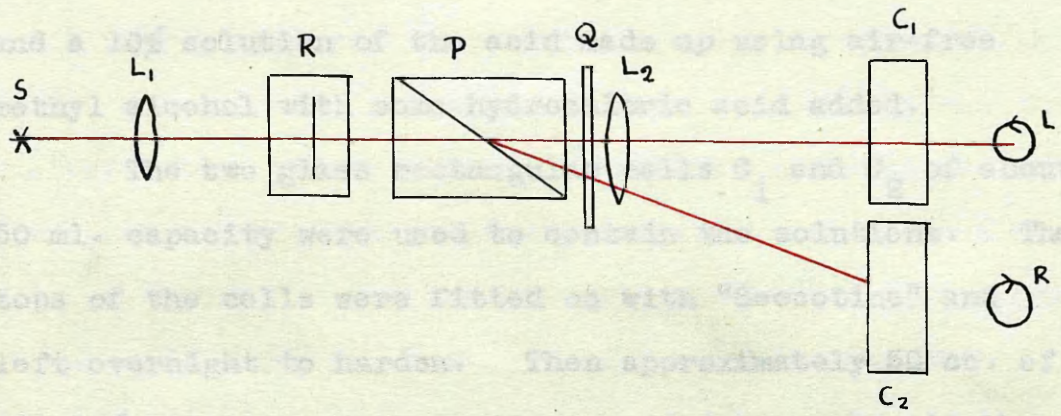
$$\alpha' = \frac{\alpha q}{2}(1-\beta)\log\frac{1}{1-\beta} \qquad \text{---- (21)}$$

it can be shown that for 60% decomposition

$$\alpha' = 0.183 \times g \times a$$
$$= 0.183 \times 0.066 \times 25$$
$$= 0.27^{\circ}.$$

It view of these results it seemed that an asymmetric photochemical decomposition could be undertaken with the hope of inducing a certain amount of rotation. This proved to be rather time consuming, but eventually rotations of $+0.11^{\circ}$ and -0.14° were obtained for a 4% solution of the blue acid itself for 60% decomposition.

The apparatus for the asymmetric photolysis is shown in the sketch



Light from the Arc Lamp S (operating at a current of 30 amps. and a voltage of 50V. D.C.) was passed through slit S_1 and water cooled filter R. The water trapped infra red radiation and heat radiation from the arc while the red glass allowed radiation above 6000 Å to pass. An image of S was formed by lens L_1 on the Rochon Prism P. This separated the light into two beams plane polarised at right angles to each other and these were circularly polarised in opposite senses by passage through the $\lambda/4$ plate (Q). This plate was so chosen that the light produced was as nearly as possible completely circularly polarised at the wavelength of maximum absorption, i.e., 6250 Å. The two circularly polarised beams were then allowed to irradiate the two cells C_1 and C_2 which contained the solution of the inactive 2-chloro-2-nitroso camphane-10-sulphonic acid.

Freshly prepared pure inactive pyridine salt was neutralised with excess concentrated hydrochloric acid and a 10% solution of the acid made up using air-free methyl alcohol with some hydrochloric acid added.

The two glass rectangular cells C_1 and C_2 of about 50 ml. capacity were used to contain the solutions. The tops of the cells were fitted on with "Seccotine" and left overnight to harden. Then approximately 50 cc. of the 10% solution of the acid was added to each cell through a small hole in the top of each cell. The cells were completely filled, care being taken to see that no air bubbles were trapped. The cells were then sealed with ground stoppers fitted with taps. Since the cells are of optical glass, it is possible to take rotation readings by placing them in the polarimeter lengthwise. This gives a length of 5 cm.

In order to decompose the acid to an extent of 60% nearly 60 hours' illumination were required. The amount of decomposition was determined by means of a photoelectric colorimeter. At the end of this time the solutions were poured into 1 dm. polarimeter tubes and rotations of $+0.11^{\circ}$ for the tube exposed to right-handed light and of -0.14° for the tube exposed to left-handed light were obtained. These figures are a good deal lower than the figures

calculated from Kuhn's Equation (0.27°) but proved nevertheless that a partial asymmetric photolysis had taken place.

The photolysis was carried a stage further. The 50 ml. solution was concentrated down to a 25 ml. and this was put into a 25 ml. cell. Radiation was continued until the concentration was about 2 per cent. Rotations for a 1 dm. tube were -0.18° for the cell exposed to left-handed light, and +0.15° for the cell exposed to right-handed light. These readings were taken at λ = 5000 Å and correspond to specific rotations of $[\alpha]_{5000}$ = -3.6° and $[\alpha]_{5000}$ = +3.0° respectively.

At this stage the solutions became greenish and white crystals were deposited on the walls of the cells. It had been hoped to extract some of the partially activated blue acid and purify it, but this was not possible owing to the accumulation of decomposition products.

PREPARATION OF COMPOUNDS.

(1). (-)-2-chloro-2-nitroso camphane.

d-Camphor was first converted into camphor oxime following the method of Auwers[72] in which the camphor, dissolved in absolute alcohol, was treated with a mixture of hydroxylamine hydrochloride and caustic soda. Provided care is taken not to add the caustic soda too quickly the method yields about 70% of pure oxime. Recrystallised from 60-80° petroleum ether, the oxime crystallised in large cubes, m.p. 115°C. $[\alpha]_D$ = -42° in ethanol. The oxime hydrochloride was prepared by dissolving the oxime in ether and passing in dry HCl gas. On crystallisation from ethanol it had m.p. = 163°C; $[\alpha]_D$ = -60°.

(-)-2-chloro-2-nitroso camphane. About 1 gm. of camphor-oxime hydrochloride was dissolved in 500 cc. sodium dried ether and placed in a flask which was fitted with inlet and outlet tubes for the passage of chlorine. The whole was cooled in ice and protected from light by means of a large can which fitted over the flask. Chlorine, dried by passing through concentrated sulphuric acid, was allowed to bubble through the solution for several hours until it had become deep green in colour. After being thoroughly saturated the excess chlorine was blown off by means of a current of air and then the ether evaporated off under

reduced pressure. The blue solid which resulted was recrystallised from methanol and gave rotation of $[\alpha]_{6000}$ = +700° as previously reported.

This was then subjected to a chromatographic analysis. The blue solid was dissolved in a little 60-80 petroleum ether and the solution allowed to pass through a column of chromatographic alumina, 1 cm. wide and 30 cm. long. After evaporation of the solvent this finally gave the blue solid whose characteristics have been discussed.

Crystallisation from methyl alcohol gave ~~for~~ a compound whose characteristics are again given below:-

m.p. 127°

$[\alpha]_{6000}$ = 964°; $[\alpha]_{7000}$ = -946°; $[\alpha]_{6700}$ = 0.0°.

ε_{max} = 12.9 at 6600 Å

$(\varepsilon_e - \varepsilon_r)_{max}$ = 1.14° at 6700 Å

g = 0.15 at 7200 Å

Analysis:- Found, C = 59.61; H = 7.61; N = 6.85%

Calculated for $C_{10}H_{16}O$ NCl

C = 59.55; H = 7.93; N = 6.93%.

The solid is extremely soluble in most of the ordinary organic solvents, but it can be recrystallised from methyl alcohol to which a little water has been added.

Oxidation by means of nitric acid or air (under the influence of red light) gave 2-chloro-2-nitro camphane[62]

m.p. 217°.

Analysis: Found, C = 54.86; H = 7.43; N = ( )

Calculated for $C_{10}H_{16}O_2NCl$, C = 55.16; H = 7.35; N = 6.43%.

Silver nitrate produced a white precipitate of silver chloride almost immediately and alkalis decolourised the solution in about an hour.

2-Chloro-2-nitroso fenchane.

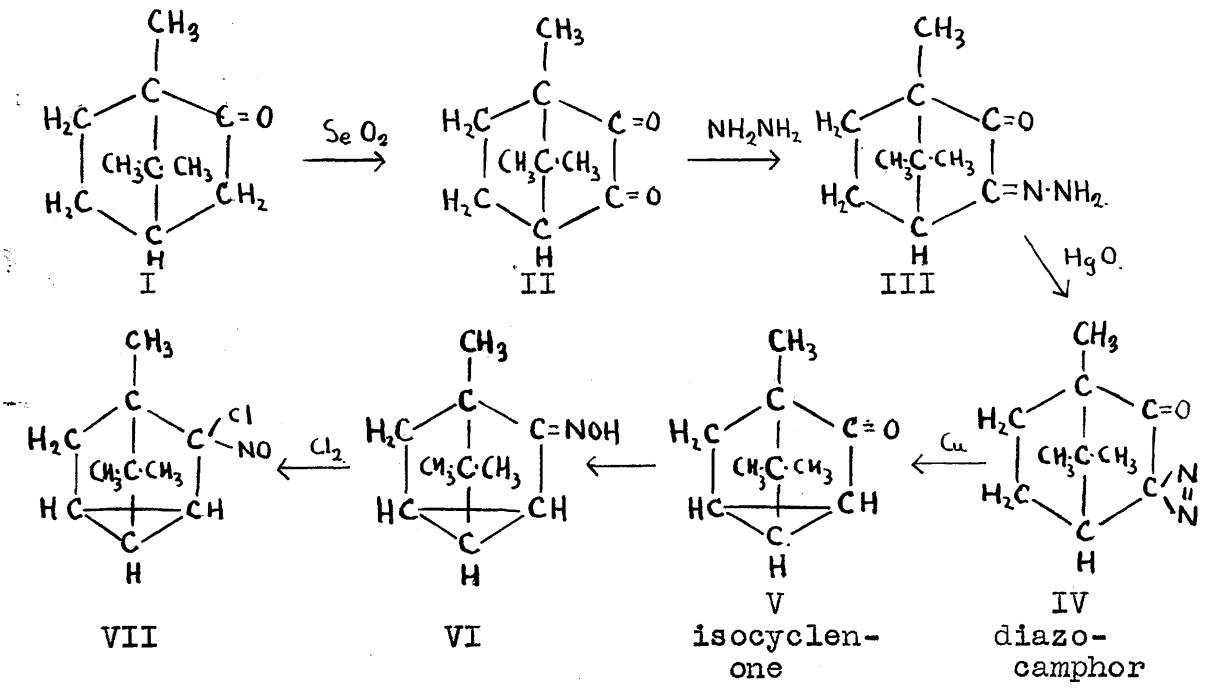
Fenchone oxime[73] was prepared in a similar manner to camphor oxime but refluxing had to be continued for about 36 hours before an appreciable amount of the oxime was formed. The yield was about 30% but the oxime could be readily crystallised from 60-80° petroleum ether. The m.p. was 163° $[\alpha]_D$ = +40° in ethanol.

(+)-2-chloro-2-nitroso fenchane.

This can be prepared as in the case of 2-chloro-2-nitroso camphane but it was found unnecessary to use the oxime hydrochloride as its use did not increase the rotatory dispersive power of the blue compound. In other details the preparation was the same. The blue solid melted between 90 - 95° and was much less stable than the corresponding camphane compound. The m.p. was 90-95° $[\alpha]_{6100}$ = -400° $[\alpha]_{6900}$ = +250°. ε_{max} = 16.5 at 6700 Å.

2-Chloro-2-nitroso isocyclene.*

The stages for the preparation of this compound from camphor are shown diagramatically as follows:-



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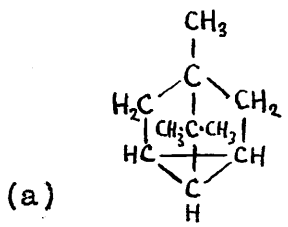
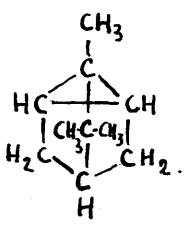
* In the literature the hydrocarbon (a) is described under various names as β-pericyclocamphane, isotricyclene, and β-bornylene, while the parent ketone is called, β-pericyclocamphenone, dehydrocamphor and isocyclenone. In view of these confusing names and of the similarity of the hydrocarbon (a) with cyclene or tricyclene (b), it is proposed to use the name isocyclene for the hydrocarbon (a) and isocyclenone for the ketone V. Thus the chloronitroso compound becomes 2-chloro-2-nitroso isocyclene using the camphor system of numbering. These names are not completely satisfactory since the termination -ene implies unsaturation and this is not the case with these compounds.



(a)



(b) cyclene

Stage I. Camphor was converted into camphorquinone according to the method of Evans, Ridgion and Simonsen[74] using selenium dioxide as oxidising agent. After drying on porous plate the product was pure enough to be used in the next stage. It may be purified if necessary from petroleum ether, m.p. 198°.

Stage II. Camphorquinone hydrazone. Stages II, III and IV follow closely the method given by Bredt and Holz[75].
22 gms. camphorquinone were dissolved in 30 cc. alcohol and heated to the boiling point, then 12 gms. of 100% hydrazine hydrate were added over a period of about 10 minutes. The mixture was heated for a further 5 minutes. It was found most advisable to use an excess of hydrazine hydrate, otherwise azocamphanone will be formed[76]. The mixture went red in colour and soon white crystals were deposited; after cooling in the refrigerator the solid was filtered. This was the α hydrazone and the red colour may be eliminated by crystallising from alcohol, m.p. 198°. Evaporating off the alcohol from the mother liquor produced a yellow solid which was the β hydrazone.

Stage III. Diazocamphor. Both hydrazones produce the same diazocamphor[75]. Oxidation of the hydrazones takes place using mercuric oxide or mercury acetamide[76].
10 gms. of hydrazone (α or β) were dissolved in 70 cc. of benzene and boiled with 15 gms. of red or yellow mercuric

oxide for 12 hours. After filtering off the mercury and unchanged oxide the benzene was evaporated off under vacuum. The diazocamphor crystallised out as yellow plates. Yield, about 7 gms. m.p. 75°. $[\alpha]_D$ = +135° in chloroform.

Stage IV. Isocyclenone (Dehydrocamphor). 1 gm. of diazocamphor was intimately mixed with 1.5 gms. copper bronze and heated in a tube into which was inserted a "cold finger". Heating very gently with a small flame caused the isocyclenone produced to appear on the cold finger as beautiful white feathery crystals, m.p. 165°. $[\alpha]_D$ = +61.5°. (Literature gives m.p. 167° $[\alpha]_D$ = +63.35°).

Stage V. Isocyclenone Oxime. This was prepared in the normal way in alcohol using potassium acetate and hydroxylamine hydrochloride in molecular proportions, refluxing for 1½ hours and leaving overnight.

The oxime melted between 65° and 124°, but recrystallisation from 60-80° petroleum ether produced a product melting at 123° C.[75].

Stage VI. 2-chloro-2-nitroso isocyclene. The blue solid was found to be very similar to the corresponding camphor compound and was made in exactly the same manner. The hydrochloride of the oxime of isocyclenone (made by passing dry HCl into the oxime dissolved in ether) was dissolved in

sodium dried ether and chlorine passed in until the solution was deep green. After blowing off the excess chlorine in a current of air the ether was evaporated off and the blue solid left recrystallised from MeOH. m.p. 135°

$[\alpha]_{6000} = +178°$ $[\alpha]_{7000} = -475°$ ε_{max} at 6600 = 15.

In other ways the blue compound behaved similarly to 2-chloro-2-nitroso camphane.

Preparation of (+)-2-chloro-2-nitroso camphane-10-sulphonic acid.

Camphor-10-sulphonic acid was first of all prepared according to the method of Reychler[71]. The acid, when drained at the pump, washed with ether and dried on porous plates, melted at 193°C. $[\alpha]_D = +25°$ in water.

Camphor-10-sulphonic acid oxime. The sulphonic acid was converted into this compound also following the procedure of Reychler. The free acid oxime had m.p. 180° $[\alpha]_D = -113°$ after being crystallised from ethanol.

2-chloro-2-nitroso camphane-10-sulphonic acid (Pyridine Salt). As already stated (p. 59) the free acid could not be made directly so that use was made of the following method which resulted in the pyridine salt being formed.

4 gms. of camphor-10-sulphonic acid oxime were dis-

solved in 10 ml. pure pyridine and cooled to -10°C in a concentrated hydrochloric acid and ice mixture. Chlorine was passed slowly into the solution taking care that the temperature did not rise, until the liquid was very deep blue green in colour. Some blue solid precipitated at this stage. The semi-solid mass was filtered and washed with ether. As a rule the solid was a sticky green mass but after drying on porous plate became bright blue. Crystallised from absolute alcohol it first appeared as blue leaflets. $[\alpha]^{18}_{6500} = +620^{\circ}$, $[\alpha]^{18}_{5600} = -550^{\circ}$, but after three crystallisations from absolute alcohol the leaflets changed to long blue needles, m.p. 155°, and the specific rotation had risen to $[\alpha]_{6600} = +800^{\circ}$, $[\alpha]_{5600} = -650^{\circ}$ $[\alpha]_{6250} = 0.0^{\circ}$.

Other characteristics of the blue salt were:-

$\varepsilon_{max} = 19.4$ at 6250 Å

$(\varepsilon_e - \varepsilon_r)_{max} = 1.27$ at 6250 Å

$g = 0.066$ at 6250 Å.

Analysis: Found, C = 49.86; H = 5.77; N = 7.87%

Calculated for $C_{15}H_{21}O_4N_2Cl$, C = 49.93; H = 5.82; N = 7.77%.

Caustic soda decolourised the salt immediately and liberated pyridine. Acids did not, however, destroy the colour. The substance was not easily oxidised by atmospheric oxygen.

(+)-2-chloro-2-nitroso camphane-10-sulphonic acid.

The free acid may be obtained by acidifying the salt with concentrated hydrochloric acid and allowing the blue liquid to stand in the refrigerator. Light blue crystals of the free acid, m.p. 65°C, can be obtained in this manner. It was found very difficult to purify the acid as it did not dissolve in the ordinary organic solvents and it was extremely soluble in water and methyl and ethyl alcohol. Measurements of rotatory dispersion gave results close to those of the pyridine salt, but the absorption was somewhat lower. ε_{max} at 6250 = 17.0.

The inactive pyridine salt of 2-chloro-2-nitroso camphane-10-sulphonic acid was prepared in a similar manner, but the starting material was inactive camphor.

SUMMARY.

In the search for a compound whose properties would fulfil all the requirements for an asymmetric photolysis the following new chloro-nitroso terpenes have been synthesised and their properties investigated:-

2-chloro-2-nitroso camphane,

2-chloro-2-nitroso fenchane,

2-chloro-2-nitroso isocyclene,

Pyridine salt of 2-chloro-2-nitroso camphane-10-sulphonic acid.

In the case of 2-chloro-2-nitroso camphane very promising results were expected, since the Rotatory Dispersion of the active compound gave the high values of $[\alpha]_{7100} = -946^{\circ}$ and $[\alpha]_{6000} = +964^{\circ}$ and the Anisotropy Factor had the remarkable value of 0.15.

When decomposition with red light was tried, however, a complication took place in which the (-) distereoisomer changed partly into the (+) isomer before normal decomposition took place and this effect would nullify to a large extent any optical activity induced by circularly polarised light in the inactive variety. This is the first instance of such a "photomutarotation" occurring in an absorption band in the visible region of the spectrum.

The same effect rendered 2-chloro-2-nitroso fenchane and 2-chloro-2-nitroso isocyclene unsuitable for asymmetric

photolysis.

The optical properties of 2-chloro-2-nitroso camphane-10-sulphonic acid are: (1) Rotations $[\alpha]_{6500} = +800^{\circ}$; $[\alpha]_{6250} = 0.0^{\circ}$ $[\alpha]_{5600} = -630^{\circ}$; (2) Anisotropy Factor 'g' = 0.066; and they are thus very similar to those of 2-chloro-2-nitroso camphane although not of such great magnitude. The acid was, however, found to be free from the above defect of "photomutarotation" when irradiated with red light, so that an asymmetric photolysis was possible even though 'g' was less than half that for 2-chloro-2-nitroso camphane. Results after 60% decomposition of a 10% solution of the free inactive acid gave rotations of $+0.11^{\circ}$ for right-handed circularly polarised light and -0.15° for left-handed light at $\lambda = 5000$. These figures are much less than the calculated figure of 0.27° derived from Kuhn's equation but are large enough to show that an asymmetric photolysis had taken place.

Thus it has been possible not only to prepare a chloro-nitroso compound at least in one active form chemically, but it has also been shown that the inactive variety can be partially resolved using only circularly polarised light. This is the first case recorded for a chloro-nitroso compound and indeed it is the first case of any compound investigated to this extent since Kuhn's work on the dimethyl amide of α-azido propionic acid.

Fig 13.

ABSORPTION, CIRCULAR DICHROISM and ANISOTROPY FACTOR of (-)-2-Chloro-2-Nitroso Camphane

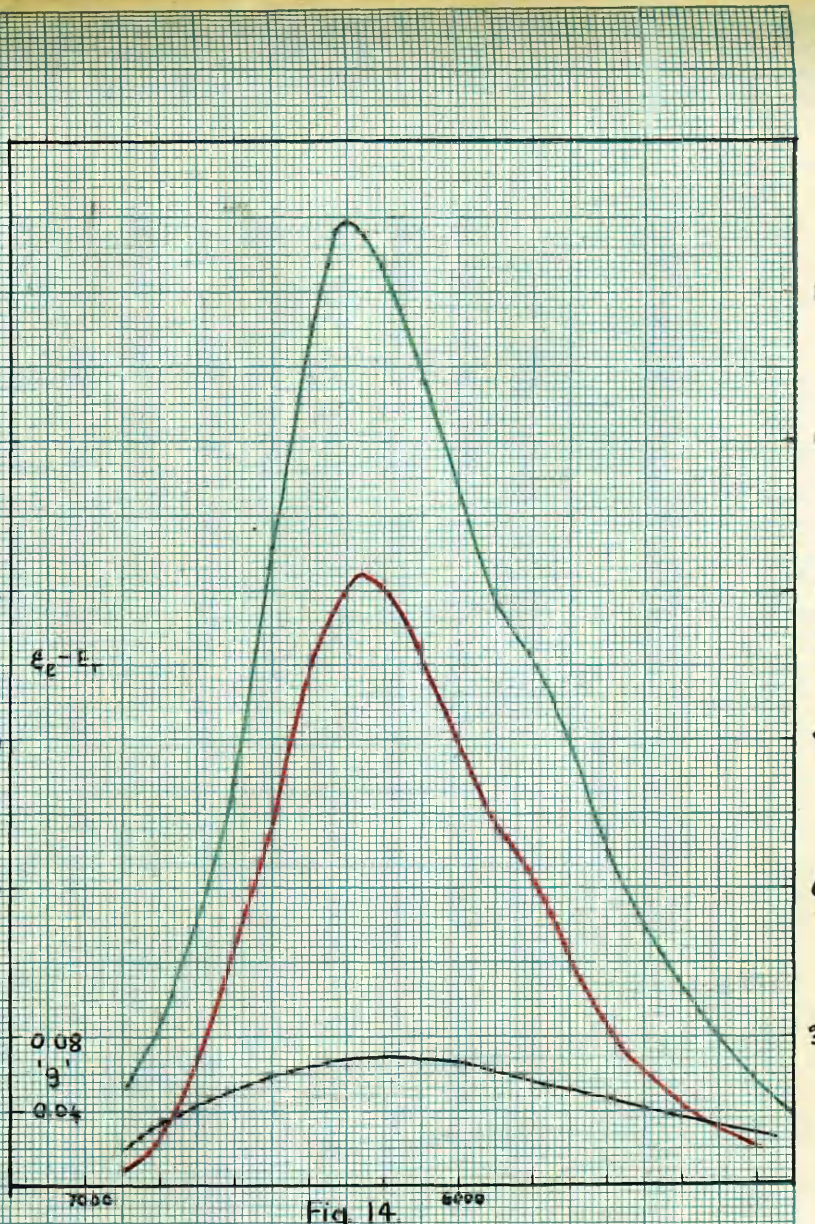


Fig. 14.

ABSORPTION, CIRCULAR DICHROISM and ANISOTROPY FACTOR Pyridine Salt of (+)-2-Chloro-2-Nitroso Camphane-10-Sulphonic Acid

PHOTO-ELECTRIC MEASUREMENT OF CIRCULAR DICHROISM AND ANISOTROPY FACTOR.

The Anisotropy Factor 'g' is a measure of the difference in absorption of right-handed and left-handed circularly polarised light in the region of an absorption band. The factor is given by $g = \frac{\varepsilon_e \sim \varepsilon_r}{\varepsilon}$ where ε is the normal Molecular Extinction Coefficient for ordinary light, ε_e and ε_r being the extinction coefficients for the two circularly polarised types.

The simplest plan would appear to be the direct measurement of Circular Dichroism ($\varepsilon_e - \varepsilon_r$) by finding directly how much one type of light was absorbed by the medium with respect to the other. Although this method was originally used by Cotton[77], his method was particularly tedious as he had to employ a visual method for comparison.

Bruhat[14] superceded this by a method which is based on the relation which Circular Dichroism bears to ellipticity. Since the two circularly polarised beams are unequally absorbed, they give rise to an elliptical vibration whose ellipticity is measured as the ratio of the major and minor axes of the ellipse. This is usually expressed as tan ϕ,

$$\tan \phi = \frac{a_r - a_l}{a_r + a_l}$$ where a_r and a_l are the amplitudes of the right and left-handed rays respectively. This equation, substituting extinction coefficients and simplifying eventually gives[78]

$$\phi = \frac{cl}{4.\log_{10}e}\ (\varepsilon_e \sim \varepsilon_r) \quad (\phi \text{ in radians})$$

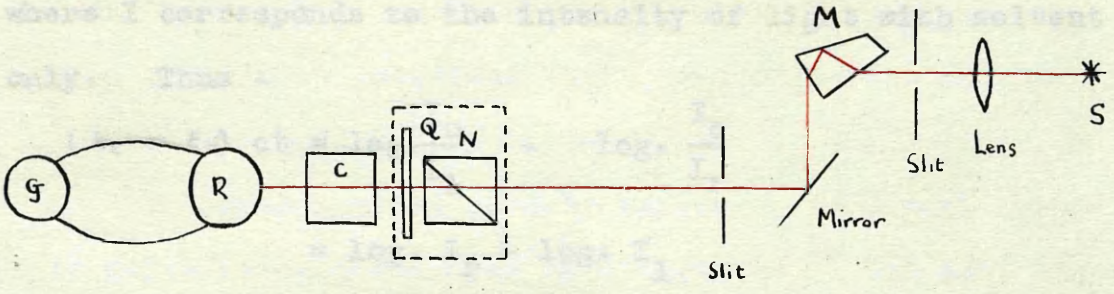
or $$\phi = \frac{cl\ (\varepsilon_e \sim \varepsilon_r)}{0.0305} \quad (\phi \text{ in degrees})$$

provided that ϕ is so small that $\tan \phi = \phi$ and that $(\varepsilon_e \sim \varepsilon_r)$ is sufficiently small that extra terms of an exponential function are not required. Thus if we know ϕ we can calculate $(\varepsilon_e \sim \varepsilon_r)$. Bruhat's method consists essentially of using an ordinary polarimeter and adding a quarter wave plate. This is rotated until the ellipticity produced by the medium is nullified; the amount of rotation then gives ϕ from which $(\varepsilon_e \sim \varepsilon_r)$ may be calculated.

From the foregoing considerations it will be seen that the method is limited to small amounts of ellipticity and this is further restricted by the half shadow angle of the polarimeter. The method is thus somewhat inaccurate, but has the advantage that only a small amount of the substance is required and also that rotations can be taken at the same time.

Modern practice is to measure absorption by photoelectric means and Dr. Mitchell, to whom the following method is due[79], suggested the use of a photoelectric cell to measure Circular Dichroism.

The first arrangement consisted of the apparatus shown in the diagram:



Light from a 36 watt bulb (S) running from a 12 volt battery supply was rendered monochromatic by a Zeiss Winkel Monochromator (M). The light was plane polarised by Glan Thompson prism (N) and then passed through a mica quarter-wave plate (Q). This plate was so chosen that the phase retardation was 90° in the region 6000 Å. The plate at 45° to the plane polarised light from the Glan Thompson prism gave right-handed circularly polarised light, while rotated to 90° from this position gave left-handed light. The solution was placed in cell (C) and the amount of light passed registered by photronic cell (R) in conjunction with galvanometer (G) which is a Cambridge Mirror Galvanometer having a resistance of 450 ohms and a sensitivity of 2550mm./μA The photronic cell (R) had a maximum sensitivity about 6200 Å so that it was admirably suited for the compounds described in this thesis. Either left- or right-handed light can be provided at will, and by removing (Q) and (N) ordinary light is given.

$(\varepsilon_\ell \sim \varepsilon_r)$ can be found from the following considerations:

$$\varepsilon_\ell ct = \log.\frac{I_o}{I_l} \qquad \text{and} \qquad \varepsilon_r ct = \log.\frac{I_o}{I_r}$$

where I corresponds to the intensity of light with solvent only. Thus -

$$(\varepsilon_e - \varepsilon_r)\, ct = \log.\frac{I_o}{I_1} - \log.\frac{I_o}{I_r}$$

$$= \log. I_r - \log. I_1$$

Values corresponding to I_r and I_1 can be read directly from the galvanometer readings.

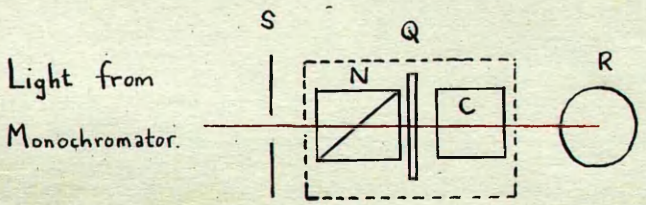
Results for the pyridine salt of 2-chloro-2-nitroso camphane 10-sulphonic acid are shown in Table XX. As much as 15 per cent difference in readings was obtained with a 3 per cent solution, giving the value of 0.065 for 'g'.

Use of "Unicam" Spectrophotometer. Owing to the relatively high concentrations required to produce appreciable differences in galvanometer readings, somewhat large slit widths on the monochromator were required using the above arrangement. Moreover, measurements could only be carried out in the region 5500 Å to 7000 Å as the sensitivity of the photocell falls off rapidly outside this region. However, the commercial instrument - the "Unicam" - requires very little light to give results for absorption spectra. In view of this desirable feature, the above Glan Thompson and Quarter wave plate arrangement was fitted to the cell carrier as shown in diagram, that is, between the exit slit of the monochromator and the photo-cells. The prism and quarter wave plate are of small dimensions - not more than an inch long - so that the arrangement is quite convenient. As

before, one position of the quarter wave plate gives right-handed circularly polarised light, and when rotated through 90^{o} gives the left-handed type.

In actual use it is only necessary to adjust the slit width for a particular wavelength until the less absorbed beam gives 100 per cent transmission, i.e., the "check" position. Switching to the other position of the quarter wave plate, the transmission of the other beam can be read directly from the Density-Transmission scale. Thus $\log \frac{I_l}{I_r}$ can be read off and by dividing by the molecular concentration ($\varepsilon_l \sim \varepsilon_r$) can be found. t = 1 cm. in this case. can be found in the normal manner with the "Unicam" and thus $g = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$ can be easily calculated.

Results for the pyridine salt of 2-chloro-2-nitroso camphane 10-sulphonic acid by the above method and that of Bruhat are given in Table XX.



In comparison with ellipticity measurements for circular dichroism, the above method has the following advantages:

As it is applicable to much larger measurements of circular dichroism, it is more accurate.

The method is much less tedious as it gives direct measurements.

It has the slight disadvantage that more concentrated solutions are required.

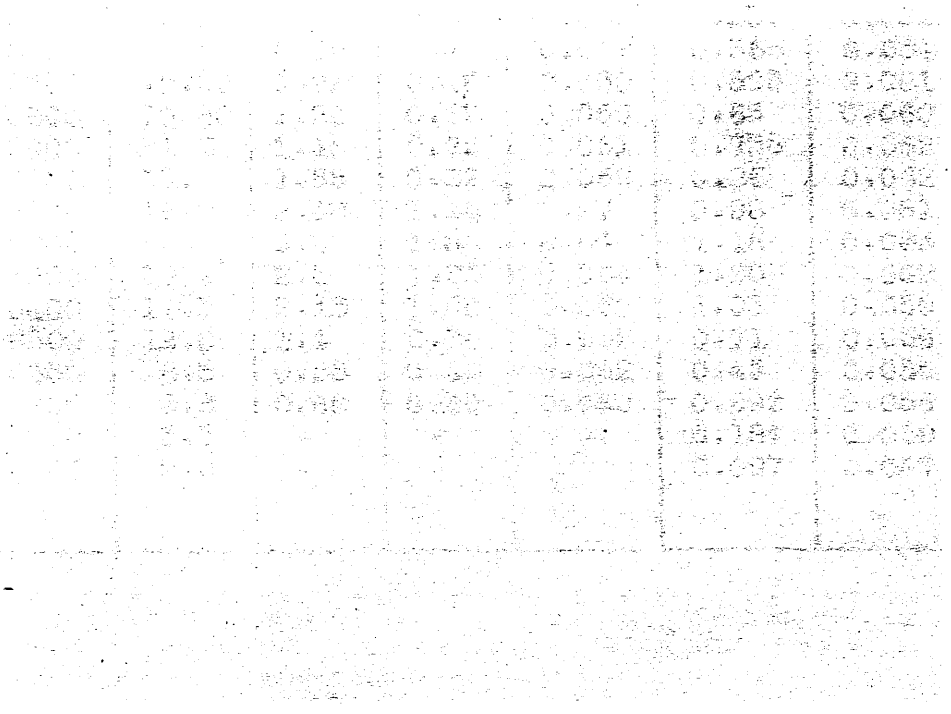


Table XX.

Comparison of Circular Dichroism and Anisotropy Factor.

(Pyridine salt of (+)-2-chloro-2-nitroso camphane-10-sulphonic acid).

(1) Ellipticity Method.

(2) Direct measurement using Photronic cell.

(3) Direct measurement using "Unicam".

		1			2		3	
λ	ε	φ	$\varepsilon_\ell - \varepsilon_r$	g	$\varepsilon_\ell - \varepsilon_r$	g	$\varepsilon_\ell - \varepsilon_r$	g.
5200	2.3	-	-	-	0.122	0.05	0.08	0.035
5400	3.9	-	-	-	0.185	0.048	0.15	0.038
5500	5.10	0.4	0.20	0.039	0.267	0.052	0.21	0.041
5600	6.7	0.65	0.32	0.048	0.365	0.054	0.30	0.045
5700	9.20	0.92	0.46	0.050	0.525	0.061	0.49	0.053
5800	10.80	1.25	0.62	0.058	0.65	0.060	0.64	0.059
5900	11.8	1.45	0.72	0.061	0.735	0.062	0.70	0.059
6000	13.8	1.65	0.82	0.059	0.86	0.062	0.86	0.062
6100	16.2	2.30	1.15	0.07	0.98	0.061	1.05	0.065
6200	18.5	2.6	1.3	0.07	1.16	0.063	1.21	0.065
6300	19.4	2.5	1.25	0.064	1.20	0.062	1.21	0.062
6400	17.3	2.15	1.06	0.062	1.03	0.059	1.05	0.061
6500	12.8	1.4	0.70	0.052	0.71	0.056	0.71	0.055
6600	8.3	0.85	0.42	0.052	0.45	0.054	0.49	0.059
6700	5.2	0.60	0.30	0.055	0.292	0.056	0.26	0.050
6800	3.3	-	-	-	0.184	0.050	0.08	0.024
6900	2.0	-	-	-	0.097	0.047	0.04	0.020

Additional paper on:

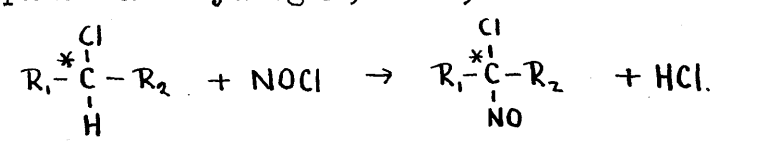
SOME PHOTOCHEMICAL EXPERIMENTS WITH NITROSYL CHLORIDE.

PHOTOCHEMICAL EXPERIMENTS WITH NITROSYL CHLORIDE.

Introduction.

In order to produce an optically active chloro-nitroso compound two methods of approach have been examined. Firstly, an inactive acid or base can be resolved by coupling it with a suitable resolving agent. This has been successfully carried out by Mitchell and Naismith[25] with γ-chloro-γ-nitroso-δ-phenyl valeric acid. They used (+) α-(2-hydroxy-1-naphthyl)benzylamine as the active base. Secondly, an active oxime may be converted into an active blue compound, but this introduces at least two asymmetric centres and complicates analysis of the Cotton Effect. It is this second approach which has yielded the results described in the earlier part of the thesis.

A third method would be to make an optically active secondary chloro compound and induce a nitroso group to replace the hydrogen, i.e.,



----- (2)

This type of reaction has not been described in the literature, but there are examples of the photochemical action of nitrosyl chloride on paraffin compounds which gave a blue colour. Lynn[53] noticed that a solution of nitrosyl chloride in n-heptane developed a blue colour on exposure

to sunlight and attributed this to the formation of a secondary nitroso derivative. The colour finally faded and he extracted an oxime from the mixture[54].

$$C_7H_{16} + NOCl \xrightarrow{-HCl} C_7H_{15}\cdot NO \text{ (blue)} \longrightarrow C_7H_{14}:NOH \text{ --- (2)}$$

Mitchell and Carson[55], investigating the action of nitrosyl chloride on n-hexane in the presence of blue light, however, found that $\beta\beta$- and $\gamma\gamma$ -chloro-nitroso hexanes were formed and that there was no evidence of the secondary nitroso compound, which if it did form, would rearrange to the oxime and this by chlorination would give the chloro-nitroso derivatives.

$$C_6H_{14} + NOCl \longrightarrow CH_3\cdot CH_2\cdot \underset{NO}{\overset{Cl}{C}} \cdot CH_2\cdot CH_3 \quad \text{and} \quad CH_3\cdot \underset{NO}{\overset{Cl}{C}} \cdot CH_2\cdot CH_2\cdot CH_3 \text{ --- (3)}$$

The question now arose - Would a secondary chloro compound when acted upon by nitrosyl chloride in the presence of blue light become blue, and if so, would it be a chloro-nitroso derivative with both groups attached to the same carbon atom? (Equation (I)). Even if this did happen with an active chloro compound, there is of course no certainty that the resulting blue product would be optically active. To test the theory it was therefore decided to experiment with the simplest member, namely, isopropyl chloride, $CH_3\cdot CHCl\cdot CH_3$. This is, of course, symmetrical but it was hoped that if results were obtained, it would give an indication as to the

possibility of similar behaviour with active compounds.

Results. (1) Isopropyl chloride.

Isopropyl chloride on being saturated with nitrosyl chloride and exposed to the blue light of a mercury lamp gave a small yield of β -chloro- β-nitroso butane, The substance does not contain an asymmetric carbon atom, but the action seemed promising, the nitroso group having entered the position required.

(2) Sec-butyl chloride.

This is the simplest type of compound, having one asymmetric carbon atom which can be prepared in the active form, so that it was decided to attempt the preparation of β -chloro- β-nitroso butane from it by the action of nitrosyl chloride in presence of light.

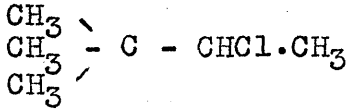
i.e., $CH_3.CH_2.CHCl.CH_3 + NOCl + h\nu = CH_3.CH_2.\overset{NO}{\underset{Cl}{C}}.CH_3 + HCl.$

If this was successful, then it was hoped to try the similar experiment but using active sec-butyl-chloride which in turn would be made from sec-butyl alcohol. When this action was attempted it was found that the mixture of sec-butyl chloride and nitrosyl chloride did indeed develop a blue colour after about 12 hours' irradiation and this when extracted gave a blue liquid boiling under reduced pressure from about 20 - 50°. Tests have shown, however, that this blue compound appeared to

be entirely $\beta\gamma$-dichloro-β-nitroso butane and it did not contain any β-chloro-β-nitroso butane as expected.

(3) Pinacolyl chloride.

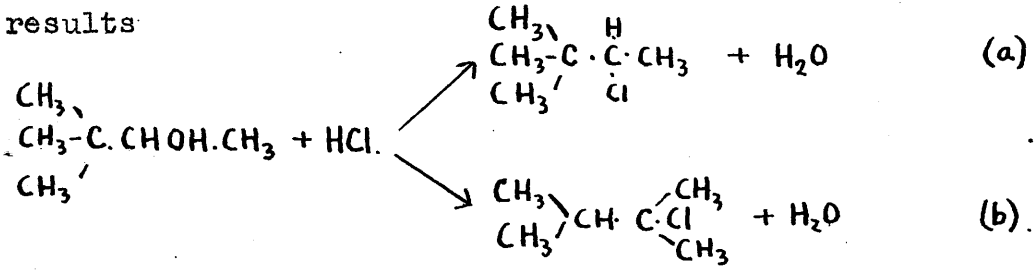
It had thus been shown that in sec-butyl chloride it is the $-CH_2-$ group which was attacked in preference to the $-CHCl-$ group. From this it would appear that a compound with no reactive group except the $-CHCl-$ was required. An example of this is pinacolyl chloride, so it was hoped



that this substance would prove useful for the reaction.

In addition, $\gamma\gamma$-dimethyl-β-chloro-β-nitroso butane is a blue solid, m.p. 121° so that if NOCl acted upon pinacolyl chloride in the presence of blue light, then a solid product should result.

Unfortunately pinacolyl chloride cannot be made in the normal manner from pinacolyl alcohol by the action of HCl, as according to Whitmore[57] a rearranged product results



Compound (b) is, of course, useless for the purpose envisaged. Pinacolyl chloride can be obtained from neohexane[57], but it

was not possible to obtain sufficient quantities of the substance to try this. In any case the possibility of obtaining active pinacolyl chloride had to be ruled out.

Negative results were obtained when nitrosyl chloride was mixed with $\beta\gamma$ dichloro butane $CH_3CHCl\ CHCl.CH_3$ and with isopropyl bromide, so that the initial success with isopropyl chloride was rather misleading and the reaction is thus very limited in its scope.

Experimental.

Tubes 6 inches long and $\frac{1}{2}$ inch wide were filled with isopropyl chloride which had been well saturated with nitrosyl chloride. These tubes had loose stoppers to prevent the oxidising action of the air, but they also had to allow for the expulsion of HCl gas from the tubes. About 9 of these tubes were placed in a tank in which water was circulating. One side of the tank was of cobalt blue glass and this side was put before a mercury lamp and irradiated for 12 hours, after which the liquid had assumed a green colour. Excess nitrosyl chloride was blown off, the liquid washed with water and it was then light blue. Fractionally distilling this liquid gave a few ml. of a blue liquid with the properties of β-chloro-β-nitroso propane,

i.e., $CH_3CHCl\ CH_3 + NOCl + HO \longrightarrow CH_3\overset{Cl}{\underset{NO}{C}}.CH_3 + HCl$

That the substance was β -chloro- β -nitroso butane was checked in the following way.

On exposing a solution of the blue liquid in methyl alcohol to sunlight a colourless liquid was obtained. This reproduced a blue colour when chlorine was passed in, showing that an oxime had been formed.

Distilling some of the colourless liquid with hydrochloric acid into a semicarbazide solution buffered with potassium acetate gave some solid melting at 187°C. No depression of melting point was noticed when acetone semicarbazone was mixed with this substance.

In order to compare the blue liquid with a sample of β-chloro- β -nitroso butane some of the latter was made by passing chlorine into a solution of acetoxime in ether. Rheinboldt and Dewald[52] have also prepared this compound, but using nitrosyl chloride instead of chlorine. After washing with water and drying over anhydrous sodium sulphate the blue liquid was separated from the ether by means of an efficient fractionating column. It boiled at 70°C at ordinary temperatures.

Reactions with sec-butyl chloride. As before, tubes containing sec-butyl chloride were saturated with nitrosyl chloride and exposed to the light of a mercury lamp (or to sunlight protected by a filter of ammoniacal copper sulphate).

A green colour developed after about 12 hours. Excess NOCl was blown off and the liquid neutralised with sodium bicarbonate solution. It was then dried over anhydrous sodium sulphate and fractionally distilled. Fractions from 22°C to 60°C were obtained at a pressure of 15 mm.

Most of the unchanged butyl chloride (coloured light blue) came over at 20°C at this pressure. In order to collect it, ice cold water was used in the condenser and a trap, surrounded by a freezing mixture of salt and ice, was inserted between the pump and the receiver. The following fractions were obtained:

	Temp.	Pressure	Quantity
(1).	22 - 30°	20 - 16 mm.	4 ml.
(2).	32 - 40°	16 - 13 mm.	1.5 ml.
(3).	50 - 60°	12 mm.	1.5 ml.

Above 50°C. the contents of the distilling flask became green in colour and there was quite a large residue. The substances left were probably dichloro compounds and nitro compounds oxidised from the nitroso compounds first formed.

Chlorine and Nitrogen Estimations gave

		Chlorine	Nitrogen
1st Fraction	22 - 30°	42.07%	3.85%
2nd Fraction	32 - 40°	44.5 %	7.65%
3rd Fraction	50 - 60°	39.2%	-

An estimation of pure β-chloro-β-nitroso butane gave N = 10.68% (Theoretical N = 11.53%).

The following table gives the percentages of Cl and N and the molecular weights of the substances which might be present.

Compound	B.P.	Mol.Weight	Cl%	N%
$CH_3 \cdot CH_2 \cdot \underset{NO}{\overset{Cl}{C}} \cdot CH_3$	24° 22 mm.	121.5	29.2	11.5
$CH_3 \cdot CH_2 \cdot \underset{NO_2}{\overset{Cl}{C}} \cdot CH_3$	51-52° 16 mm.	137.5	25.8	10.18
$CH_3 \cdot CHCl \cdot \underset{NO}{\overset{Cl}{C}} \cdot CH_3$	50° 20 mm.	156	45.5	8.9
$CH_3CHCl \cdot \underset{NO_2}{\overset{Cl}{C}} \cdot CH_3$	-	172	41.5	8.13
$CH_3 \cdot CHCl \cdot CHCl \cdot CH_3$	115-120°	127	55.9	-

Considering these, it would seem that by far the greater proportion of the blue liquid is $\beta\gamma$-dichloro-β-nitroso butane, $CH_3 \cdot CHCl \cdot \underset{NO}{\overset{Cl}{C}} \cdot CH_3$. It was thought that the sec-butyl chloride which had distilled over might have contained a proportion of β-chloro-β-nitroso butane, but when the pure dichloro nitroso compound was dissolved in sec-butyl chloride and distilled, the distillate was again coloured blue, so that this test was of negative value.

Some of the blue liquid was dissolved in methyl alcohol and exposed to sunlight in a sealed tube. After a few hours the liquid became colourless, but the blue colour was reproduced when chlorine was passed in. On distilling some of the colourless liquid with hydrochloric acid and collecting the distillate in a solution of semicarbazide hydrochloride which had been buffered with potassium acetate, a semi-carbazone having the properties of that of 3-chlor butan-2-one was produced. This substance melted at 139° and it had the peculiar property that its colour became red before it melted.

In order to compare the blue liquid with pure $\beta\gamma$-dichloro-β-nitroso butane, a pure specimen of this compound which appears to be a new one was prepared.

Preparation of $\beta\gamma$-dichloro-β-nitroso butane. The ketone 3-chlor-butan-2-one was prepared by the method of Curd and Robertson[58], the starting material being ethyl aceto acetate and the sequence of reactions being

$$CH_3CO.CH_2COOEt + CH_3I + NaOEt \longrightarrow CH_3.CO.\underset{\displaystyle CH_3}{\underset{|}{CH}}.COOEt$$

$$CH_3.CO.\underset{\displaystyle CH_3}{\underset{|}{CH}}.COOEt + SOCl_2 \longrightarrow CH_3.CO.\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}.COOEt$$

$$CH_3.CO.\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}.COOEt + H_2SO_4 \longrightarrow CH_3.CO.CHCl.CH_3$$

To this ketone was added a solution of hydroxylamine in alcohol. The mixture after standing a few hours was cooled in ice and chlorine passed in (cf. Rheinboldt and Dewald[52]). A blue liquid soon formed. It was extracted with ether, washed and dried over anhydrous sodium sulphate. It distilled under reduced pressure at 50°C.

Some of the $\beta\gamma$-dichloro-β-nitroso butane was dissolved in methyl alcohol and exposed in a sealed tube to sunlight. After 4 hours the liquid was colourless. On repassing chlorine, a blue colour was produced. When distilling with HCl and the aqueous distillate added to a solution of potassium acetate and semicarbazide hydrochloride, a precipitate formed. This became red on heating and melted at 139°C.

The pure $\beta\gamma$-dichloro-β-nitroso butane thus behaved in an exactly similar manner to the blue liquid from sec-butyl chloride.

Summary.

The photochemical action of nitrosyl chloride on compounds of the type $R_1 - \overset{Cl}{\underset{H}{C}} - R_1$ has proved to be of very limited application. Although isopropyl chloride gave β-chloro-β-nitroso propane, sec-butyl chloride gave not the desired β-chloro-β-nitroso butane but βγ-dichloro-β-nitroso butane. Other compounds such as isopropyl bromide and βγ-dichloro butane did not react. The possibility of using pinacolyl chloride has been discussed and has been ruled out owing to the inability of obtaining the substance readily and in its active form.

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